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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LEIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MkhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. - Publisher.

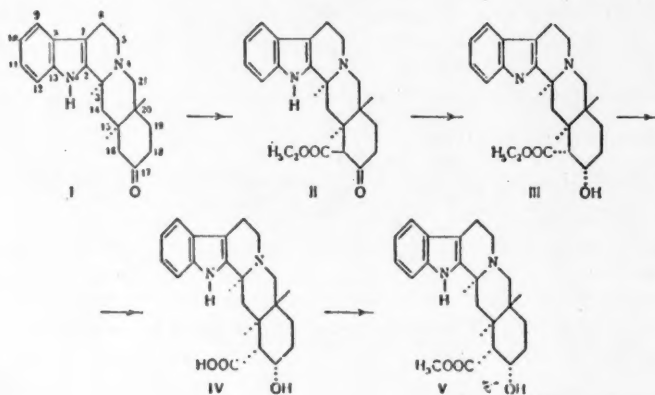
SYNTHESIS OF THE ALKALOID YOHIMBINE

L. A. Aksanova and N. A. Preobrazhensky

(Presented by Academician I. N. Nazarov, June 17, 1957)

In our previous communication [1] on investigations in the field of the synthesis of the alkaloid yohimbine (V), we described the preparation of apoyohimbine from yohimbine and an ester of formic acid. This solved one of the basic problems of the synthetic preparation of the active principle of the bark of *Corynanthe johimbe* — reproduction of the hydrogenated E ring, which corresponds in structure and location of atoms to the natural yohimbine alkaloid (V). However, our synthesis did not make it possible to progress to the preparation of yohimbine, since the synthesis of 16- α -carbomethoxy-17- α -hydroxyyohimban (V) from 16- α -carbomethoxy-16-yohimbene is very difficult.

In the present work, we established that yohimbone (I) reacts with diethyl carbonate with the formation of carboethoxyyohimbone (II).



By reduction of the resulting ester to III, subsequent saponification of III to IV, and esterification of IV, the methyl ester of yohimbolcarboxylic acid, the alkaloid yohimbine (V), was obtained.

The reaction of ethyl carbonate with the yohimbone base (m. p. 296-298°) (I) in the presence of sodium alcoholate and in a dry benzene medium proceeds slowly, and the heat required for completion of the reaction causes some saponification and decomposition of the material. We were unable to obtain analytically pure material by reacting dimethyl carbonate and yohimbone under these conditions. The best results were obtained by carrying out the condensation of yohimbone with a large excess of diethyl carbonate by stirring for 3-4 days at 18-20°. After separation of the unreacted yohimbone, removal of the solvent under vacuum, and treatment of the condensation product with water, the sodium salt of the enol form was decomposed with acetic acid. The

precipitate was extracted with chloroform. The ethyl yohimbonecarboxylate (II) is a yellowish, crystalline substance. The melting point of the unpurified base was 98-105°. The yield was 60% of theoretical.

Hydrochloride, m. p. 241-243° (from 70% ethyl alcohol).

Found %: C 65.68, 65.33; H 6.20, 6.34; N 6.72, 6.88. $C_{22}H_{27}O_3N_2Cl$. Calculated %: C 65.59; H 6.78; N 6.95.

The ethyl yohimbonecarboxylate (II) was subjected to catalytic hydrogenation in the presence of platinum oxide in a benzene-ethyl alcohol medium at a temperature of 35-40° and 80 atm. pressure. The reduction product did not change color in ferric chloride solution. The yield of ethyl yohimbolcarboxylic acid (III) was 93% of theoretical.

M. p. 178-184° (decomposition) (from 60% ethyl alcohol).

Found %: C 71.73, 71.72; H 7.47, 7.72; N 7.58, 7.97. $C_{22}H_{29}O_3N_2$. Calculated %: C 71.74; H 7.61; N 7.61.

Hydrochloride, m. p. 275-280° (decomposition) (repeated recrystallization from 70% ethyl alcohol).

Found %: C 65.08, 65.20; H 7.17, 7.14; N 7.91, 6.92. $C_{22}H_{29}O_3N_2Cl$. Calculated %: C 65.26; H 7.22; N 6.92.

This hydrochloride of the base III was identical with the ethyl ester of yohimbic acid obtained by saponification of the natural alkaloid yohimbine with potassium carbonate in 70% methanol and subsequent esterification with ethyl alcohol.

Hydrochloride melting point 279-281° (decomposition) (from 70% ethyl alcohol).

Found %: C 65.23, 65.18; H 7.25, 7.32; N 6.96, 6.84. $C_{22}H_{29}O_3N_2Cl$. Calculated %: C 65.26; H 7.22; N 6.92.

A mixed sample of the hydrochlorides of the ethyl esters of the natural and synthetic yohimbolcarboxylic acids melted without depression of the melting point [m. p. 277-280° (decomposition)].

The natural alkaloid yohimbine is the methyl ester of 16- α -carboxy-17- α -hydroxy-yohimban (V). Therefore, we carried out the conversion of the ethyl ester of 15-carboxy-17-hydroxy-yohimban (III), obtained by us from yohimbone, to the methyl ester. With this aim, the ethyl esters of the isomeric β -hydroxyacids were saponified with a solution of potassium carbonate in a medium of 60% methanol. The acid separated.

M. p. 245-249° (decomposition) (from water).

Found %: C 70.48, 70.20; H 7.08, 6.81; N 8.20, 8.33. $C_{20}H_{24}O_3N$. Calculated %: C 70.59; H 7.06; N 8.24.

After esterification of the β -hydroxy acid IV with methanol saturated with hydrogen chloride, we obtained the hydrochloride of methyl yohimbolcarboxylate (V). This compound was purified through the base (aqueous ammonia), the tartrate (alcoholic solution of (+)-tartaric acid), again the base (aqueous ammonia), and crystallization from 70% ethyl alcohol. The methyl yohimbolcarboxylate was obtained as acicular crystals.

M. p. 234-236.5° (decomposition) (sinters 226°).

Found %: C 71.10; H 7.23; N 7.63. $C_{21}H_{26}O_3N_2$. Calculated %: C 71.14; H 7.34; N 7.91.

Hydrochloride, m. p. 299-302° (sinters 294°).

Found %: C 64.42; H 6.92; N 6.86. $C_{21}H_{27}O_3N_2Cl$. Calculated %: C 64.50; H 6.91; N 7.17.

A mixed sample with the hydrochloride of the natural alkaloid yohimbine (m. p. 298-300°) showed no depression of the melting point.

Thus, our work completes the total synthesis of the alkaloid yohimbine, since previously this synthesis has been carried only to the stage of yohimbone [2] and apoyohimbine [1].

* As in original — Publisher's note.

For confirmation of the location of the carbomethoxy and hydroxyl groups in the E ring of the natural and synthetic yohimbinines, we made use of the method used by G. Fodor to establish steric configuration in a number of tropan alkaloids [3].

Our synthetic ethyl yohimbolcarboxylate (III) was reduced with lithium aluminum hydride in dry tetrahydrofuran to yohimbyl alcohol (VI). The yield was 39.5% of theoretical. M. p. 194-199°.

Found %: C 73.53, 73.41; H 7.77, 7.68; N 8.59, 8.63. $C_{20}H_{28}O_2N_2$. Calculated %: C 73.57; H 7.97; N 8.59.

Hydrochloride, m. p. 282-284° (from 70% ethyl alcohol).

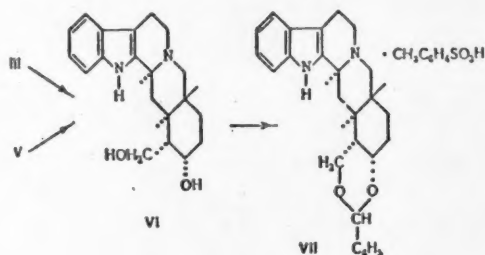
Found %: C 66.20; H 7.73; N 7.60. $C_{20}H_{27}O_2N_2Cl$. Calculated %: C 66.21; H 7.45; N 7.72.

We also prepared yohimbyl alcohol by reduction of yohimbine with lithium aluminum hydride under similar conditions.

Hydrochloride, m. p. 283-285°.

Found %: C 66.60; H 7.46; N 7.75. $C_{20}H_{27}O_2N_2Cl$. Calculated %: C 66.21; H 7.45; N 7.72.

A mixed sample of these substances showed no depression of the melting point.



Further, reaction of the synthetic yohimbyl alcohol (VI) with benzaldehyde in the presence of p-toluenesulfonic acid gave the p-toluenesulfonate of the benzylidene derivative (VII).

M. p. 283-286°.

Found %: C 69.51, 69.54; H 6.43, 6.73; N 4.46, 4.55. $C_{24}H_{38}O_5N_2S$. Calculated %: C 69.62; H 6.48; N 4.78.

The reaction of the yohimbyl alcohol (VI) prepared by reduction of the natural alkaloid yohimbine (V) with benzaldehyde under the same conditions gave the analogous cyclic acetal.

Found %: C 69.50, 69.86; H 6.15, 6.52; N 4.61, 4.73. $C_{24}H_{38}O_5N_2S$. Calculated %: C 69.62; H 6.48; N 4.78.

A mixed sample of the synthetic p-toluenesulfonate of the benzylidene derivative (m. p. 283-285°) with the p-toluenesulfonate of the cyclic acetal synthesized from the natural alkaloid yohimbine (m. p. 282-285°) showed no depression of the melting point.

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SELECTIVE HYDROGENATION OF MONOSACCHARIDES AND POLYHYDRIC ALCOHOLS

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I. As shown in the scientific and patent literature (for a review, see [1]) and also by our experiments ([1], of [2]), the following reactions proceed in aqueous solution over Ni catalysts at 150-300 atm. of hydrogen.

1. At 120-130°, monosaccharides are hydrogenated practically completely to the corresponding polyhydric alcohols: xylose to xylitol, glucose to sorbitol, etc.

2. With an increase in temperature, hydroxyl groups are split from the alcohols, the hydroxyl groups at the ends being removed first; thus, 1,2-propylene glycol is formed from glycerin, and isopropyl alcohol is formed from the former. Higher alcohols lose hydroxyl groups more difficultly than lower alcohols.

3. Still more difficultly, uronic acids are formed in amounts up to several percent from monoses with an insufficiency of hydrogen (for example, with insufficient stirring), thereby creating an acid reaction medium.

4. Cleavage of C-C bonds, most frequently in the center of the molecule, partially competes with these reactions, but in general proceeds at a higher temperature (220-230°). Thus, under specific conditions, propylene glycol and glycerin are formed from sorbitol.

Depending on the structure of the molecules, the indicated succession of reactions is sometimes somewhat disrupted, but the general rule is very clearly apparent from experimental material.

II. Among the works devoted to the mechanism of these reactions, two are of interest: Schmidt [3] and, particularly, Natta, Rigamonti and Beati [4]. Both deal with Ni catalysts. Schmidt [3], on the basis of a large amount of data, concludes that rupture of the C-C bond proceeds in the 3,4-position during hydrogenolysis of carbohydrates. He explains this by the formation at 200° of pentitols and hexitols which partially dehydrogenate reversibly to pentoses and hexoses, the aldehyde group of which enolizes, resulting in the strengthening of the neighboring C-C bond and weakening and subsequent cleavage of the C-C bond next to it. The explanation of Schmidt is refuted by the improbability of any appreciable dehydrogenation at a hydrogen pressure of 150-300 atm. and 220°.

Natta, Rigamonti, and Beati [4] consider that the reaction first occurring is that for which the free energy change (at 298°K), ΔF , is lower. However, in the first place, this has no theoretical basis, and, in the second place, it is justified by experiment only for isolated series of compounds and not for the general case. If this rule of the Italian authors was always right, then, for example, in the hydrogenation of hexitol, first the hydroxyl groups would split off (since splitting off of a primary hydroxyl corresponds to $\Delta F = -22,000$ cal/mole, and that of a secondary hydroxyl to $\Delta F = -18,000$ cal/mole); glycerin absolutely could not be formed (since here $\Delta F = -4,600$ cal/mole). This is completely contrary to experiment.

III. The multiplet theory of catalysis [5] is applied below to the reactions under consideration; this theory has given the correct succession of hydrogenation and hydrogenolysis of various compounds [5], among them derivatives of furan [6], triptycene [7], and organic peroxides [8].

The multiplet theory separates the reacting atoms in the molecule into a so-called index, a doublet group:



These atoms come into contact with the catalyst K (though not necessarily simultaneously). Moreover, the reaction rate is higher the better structural and energy correspondence is maintained. In the present case, structural correspondence in fact occurs, as was shown earlier for these same atoms [5]. Energy correspondence is observed more completely the lower the energy barrier ($-E$), or, in other words, the higher the value

$$E = -Q_{AB} - Q_{CD} + (Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}), \quad (2)$$

where Q is the bond energy, and A, B, C, D, and K are the same atoms as in Equation (1).

TABLE 1
Calculated Comparative Ease, E , of the Occurrence of Reactions
Over Ni (Effect of the Nature of the Atoms in the Index)

No.	Type of reaction	Index of reaction	$E_{\text{calc.}}$ cal/mole
1	Hydrogenation of carbonyl bond of mono-saccharides	$\begin{array}{c} >C-H \\ \\ O-H \end{array}$	$-10,000$
2	Reduction of alcohol group, hydrogenolysis of C-O bond	$\begin{array}{c} \geq C-H \\ \\ O-H \end{array}$	$-17,000$
3	Cannizzaro reaction, formation of uronic acids	$\begin{array}{c} >C-H \\ \\ O-C_2H_5 \end{array}$	$-32,000$
4	Rupture of carbon chain of alcohol, hydrogenolysis of C-C bond	$\begin{array}{c} >C-H \\ \\ \geq C-H \end{array}$	$>-48,000$

Thus, the greater E is, the greater the reaction rate. It should be emphasized that E — the kinetic value — is the energy of formation of the multiplet activated complex (equal to $\frac{1}{4}$ of the energy of activation with the opposite sign), and not the heat of the reaction, which is considered in Berthelot's principle, or the ΔF of the Italian authors.

Taking the indices of the reactions which are of interest to us, and substituting in Equation (2) the values of Q (a summary of which is given in [9]) we obtain, for a Ni catalyst, the results presented in Table 1. For rupture of a C-C bond, $E > -48,000$ cal/mole, since here these bonds undergo a well-known significant weakening owing to the presence of hydroxyls by them. This weakening will yield to precise quantitative calculation when measurements of the individual bond energies have been made. However, the succession of reactions in Table 1 corresponds to experiment (see Paragraph I), in contrast to the theoretical results of previous authors (see Paragraph II).

As a by-product of the calculations, the data of Table 1 show clearly that, in the case of monosaccharides, the open, oxo form must be hydrogenated first, for which $E = -10,000$ cal/mole, and not the cyclic form, which predominates in solution, for which E is less ($E = -17,000$ cal/mole). Moreover, as shown by the hydrogenation

of acetals over Ni [10], the second oxygen atom in the α -position does not too greatly weaken the C-O bond.

IV. The effect of structure on the rate of a reaction of a given type is due to the effect of substituents along the side. Thus, the introduction of substituents, for example, at atom A in Formula (1), affects Q_{AB} and Q_{AK} in Equation (2). This changes E [11] and, consequently, the reaction rate. Calculation gives the following.

Substituting the values of A from Equation (2) into the equation for the heat of reaction $u = Q_{AD} + Q_{BC} - Q_{AB} - Q_{CD}$ [see Formula (1)] and into the well-known thermodynamic equation $\Delta F = -u - T\Delta S$, where S is entropy, we obtain

$$\begin{aligned}\delta E &= \delta Q_{AK} - \delta Q_{AB}, \\ \delta u &= \delta Q_{AD} - \delta Q_{AB}, \\ \delta \Delta F &= -\delta u - T\delta \Delta S.\end{aligned}\quad (3)$$

From Equation (3), it follows that if a substituent is introduced at A, then

$$\delta E = -\delta \Delta F - (T\delta \Delta S - \delta Q_{AD} + \delta Q_{AK}).\quad (4)$$

For condensed (i.e., solid and liquid) systems, $\delta \Delta S$ must be small; the values of δQ_{AD} and δQ_{AK} are also small in comparison with $\delta \Delta F$ and, moreover, enter into Equation (4) with different signs. Therefore, if gases are not liberated during the reaction, then in Equation (4) the value in parentheses must be small. Hydrogen is present in the system in all cases. On the basis of the above

$$\Delta E \cong -\delta \Delta F.\quad (5)$$

Thus, the reaction must be the more rapid the greater the decrease in the free energy of the reaction, $\delta \Delta F$, caused by the substituent. Equations (4) and (5) differ from the rule of Natta, Rigamonti and Beati, first of all, in that they relate to the variation in $\delta \Delta F$, and not in ΔF itself. Moreover, Equations (4) and (5) have a theoretical basis.

TABLE 2

Calculated Relative Ease, δE of the Occurrence of the Hydrogenolysis of a C-O Bond In Polyhydric Alcohols Over Ni (Effect of Substituents on Reaction 2, Table 1)

No.	Reaction	$\delta E = -\delta \Delta F_{\text{calc.}}$ cal/mole
1	Hexitol \rightarrow methylpentitol + H_2O	2600
2	Pentitol \rightarrow methylerythritol + H_2O	2600
3	Erythritol \rightarrow methylglycerin + H_2O	2700
4	Erythritol \rightarrow 1,2,4-butenetriol + H_2O	-300
5	Glycerin \rightarrow 1,2-propylene glycol + H_2O	2100
6	Glycerin \rightarrow 1,3-propylene glycol + H_2O	-1300
7	Propylene glycol \rightarrow n-propyl alcohol + H_2O	-1600
8	Propylene glycol \rightarrow isopropyl alcohol + H_2O	2500
9	Ethylene glycol \rightarrow ethyl alcohol + H_2O	-2700

The values of $\delta \Delta F$ presented in Tables 2 and 3 for the hydrogenolysis of the compounds under consideration were calculated from the free energies of formation according to the data of Parks and Huffman [12], just as were the values of ΔF of the Italian authors [4]. Calculation of $\delta \Delta F$ was based on the average of the extreme values. Reactions giving gaseous methane were not included in Tables 2 and 3 for reasons indicated above.

It can be seen that the succession of reactions according to $\delta \Delta F$ are in agreement with experiment. Preferential rupture of the carbon chain actually occurs in the middle (see Nos. 1, 4, and 12, Table 3), and is explained by the fact that the value of Q_{C-C} is less here, increasing toward the end of the chain. Primary hydroxyls are split off more easily than secondary (see Nos. 3 and 5, Table 2). In Reaction 4, Table 1, the effect of hydroxyl groups is summarily taken into account by the statement that $E > -48,000$ cal/mole. However, it is clear that the greater the accumulation of hydroxyl groups, the greater the weakening of the C-C bond must be. This consideration, in contrast to that of the Italian authors, explains why, in the case of the higher alcohols - pentitols and hexitols - rupture of the C-C bond precedes splitting off of hydroxyls, while in lower alcohols - glycerin and ethylene glycol - the reverse occurs. Therefore, the formation of 1,2-propylene glycol from glycerin (see No. 5, Table 3) is normal, and the formation of the 1,2-isomer, and not the 1,3-isomer, (see Nos. 5 and 6, Table 2) is in agreement with experiment. This explains why a mixture of propylene glycol and glycerin of unlike composition is obtained in the hydrogenolysis of sorbitol.

TABLE 3
Calculated Relative Ease, δE , of the Occurrence of Hydrogenolysis of C-C Bonds in Polyhydric Alcohols Over Ni (Effect of Substituents on Reaction 4, Table 1)

No.	Reaction	$\delta E = -\delta \Delta F$ calc. cal/mole
1	Hexitol \rightarrow 2 moles glycerin	1200
2	Hexitol \rightarrow erythritol + ethylene glycol	400
3	Hexitol \rightarrow methanol + pentyne	160
4	Methylpentitol \rightarrow glycerin + Propylene glycol	700
5	Methylpentitol \rightarrow methylglycerin + ethylene glycol	500
6	Methylpentitol \rightarrow methylerythritol + methanol	-1060
7	Pentitol \rightarrow ethylene glycol + glycerin	1100
8	Pentitol \rightarrow erythritol + methanol	-40
9	Methylerythritol \rightarrow ethylene glycol + propylene glycol	600
10	Methylerythritol \rightarrow ethanol + glycerin	-600
11	Methylerythritol \rightarrow methanol + methylglycerin	-40
12	Erythritol \rightarrow 2 molecules ethylene glycol	1200
13	Erythritol \rightarrow glycerin + methanol	200
14	Methylglycerin \rightarrow ethanol + ethylene glycol	-1200
15	Methylglycerin \rightarrow methanol + propylene glycol	200
16	Glycerin \rightarrow ethylene glycol + methanol	-40

By the very nature of the case, the values of δE from Tables 2 and 3 should be added to E from Table 1. In this lies the chief distinction from the methods of calculation of previous authors, permitting avoidance of the contradictions to experiment indicated in Paragraph II. The effect of the nature of the catalyst is taken into account by the components with the subscript K in Equations (2) and (4).

Thus, application of the multiplet theory has excellent prospects in the field of the hydrogenation of monosaccharides and polyhydric alcohols, as may be seen from Tables 1 and 2; we plan further treatment of these questions.

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INVESTIGATION OF THE CONDITIONS OF FORMATION AND OF THE
STABILITY OF COMPLEX OXALATE COMPOUNDS OF
Pu (III) IN AQUEOUS SOLUTIONS

A. D. Gelman, N. N. Matorina, and A. I. Moskvín

(Presented by Academician I. I. Chernyaev, June 24, 1957)

According to literature data, Pu(III) exhibits considerably less tendency toward complex formation than does Pu(IV). Hindman and co-workers [1] investigated the effect of a change in concentration of perchloric, hydrochloric, nitric, and sulfuric acids on the absorption spectra of Pu(III). Although changes in the spectra were small, nevertheless the tendencies of the various acids toward complex formation with Pu(III) were arranged by these authors in the following order: $\text{ClO}_4^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-}$.

The data of Thomas and Werner [2] on the preparation of Pu(III) oxalate complexes were regarded with some doubt by Hindman, since the color of the solution (green instead of bluish) and the conditions under which the experiments were carried out demanded additional proof that the oxalate complexes were formed from Pu(III), and not from Pu(IV).

By means of a spectrophotographic method, we studied the stability toward oxidation by atmospheric oxygen of solutions of oxalate, citrate, carbonate, and ethylenediamine tetraacetate complexes of Pu(III). As a result of this investigation, it was possible to show that the doubts of Hindman with respect to the data of [2] were justified. The complex Pu(III) compounds, which had a typical azure-blue color, were stable toward oxidation by atmospheric oxygen only when the experiments were carried out in an atmosphere of nitrogen or in the presence of a very strong reducing agent.

The absorption spectra of the above-indicated Pu(III) complex compounds had very characteristic absorption maxima at wave lengths of approximately 565, 605, 780-790, 905-910, and 1090 m μ , and were similar to the absorption of a nitric acid solution of Pu(III). Such similarity in the absorption spectra is in agreement with the proposal of Hindman [3] that complex formation cannot give rise to appreciable changes in the absorption spectra of Pu(III) in view of the strong shielding of the 5f electrons (the absorption spectra were measured at room temperature in the region of 400-1100 m μ with a domestically produced SF-4 spectrophotometer).

Having established the conditions under which Pu(III) oxalate complexes are stable toward oxidation by atmospheric oxygen, we decided to determine the composition and dissociation constants of complex ions of Pu(III) with various complex formers. Various physicochemical methods [4-14] are widely used to determine the composition and stability of complex compounds. In the present work are presented the results obtained in a study of Pu(III) oxalate complexes by the solubility method (at a pH of approximately 8) and by the ion exchange method (at pH of 1.4-3.0). It should be noted that these methods do not permit establishment of the true coordination number of the central atom; however, they do make it possible to determine the ratio of the central atom to the ligands and to calculate the dissociation constants of the complex ions formed.

The solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in aqueous solutions of $\text{K}_2\text{C}_2\text{O}_4$ (0.01-2.4 mole/liter) at a temperature of 20° and constant ionic strength of the solution was initially determined. It was shown by preliminary experiments that stirring for 4-6 hours was quite sufficient to establish equilibrium between the solution and the

solid phase. A continuous stream of nitrogen was passed through the solution to prevent oxidation of the Pu (III). The plutonium contents of the solutions were determined by the radionetric method. The results of the solubility determinations are presented in Table 1.

TABLE 1
Solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in Aqueous
Solutions of $\text{K}_2\text{C}_2\text{O}_4$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$

$\text{K}_2\text{C}_2\text{O}_4$ conc., moles/ liter	Sol. Pu (III) oxalate, moles/ liter	$(\text{NH}_4)_2\text{C}_2\text{O}_4$ concn., moles/ liter	Sol. Pu (III) oxalate, moles/ liter
0.01	$3.53 \cdot 10^{-8}$	0.07	$2.02 \cdot 10^{-4}$
0.025	$7.54 \cdot 10^{-8}$	0.13	$2.90 \cdot 10^{-4}$
0.05	$1.00 \cdot 10^{-4}$	0.225	$4.70 \cdot 10^{-4}$
0.075	$1.09 \cdot 10^{-4}$	0.28	$5.66 \cdot 10^{-4}$
0.10	$1.55 \cdot 10^{-4}$	0.35	$6.90 \cdot 10^{-4}$
0.2	$2.7 \cdot 10^{-4}$	0.41	$8.10 \cdot 10^{-4}$
0.3	$4.04 \cdot 10^{-4}$	0.49	$9.75 \cdot 10^{-4}$
0.6	$1.01 \cdot 10^{-3}$	0.56	$1.14 \cdot 10^{-3}$
0.8	$1.71 \cdot 10^{-3}$	0.62	$1.50 \cdot 10^{-3}$
0.9	$2.27 \cdot 10^{-3}$	0.66	$2.05 \cdot 10^{-3}$
1.2	$3.46 \cdot 10^{-3}$	0.70	$2.25 \cdot 10^{-3}$
1.51	$5.91 \cdot 10^{-3}$		
1.81	$8.45 \cdot 10^{-3}$		
2.00	$1.06 \cdot 10^{-2}$		
2.41	$1.87 \cdot 10^{-2}$		

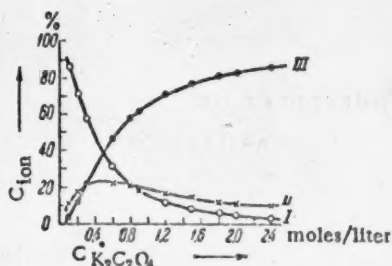
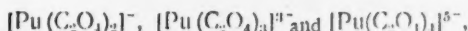


Fig. 1. Effect of the concentration of the $\text{C}_2\text{O}_4^{2-}$ ion on the concentration of the complex ions: I) $[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$, II) $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{3-}$, III) $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{5-}$.

The solubility products, L_p , of Pu (III) oxalate, calculated from data on the solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in water at 20 and 70°, are respectively, $1.62 \cdot 10^{-25}$ and $2.52 \cdot 10^{-22}$.

On the basis of the results obtained, the compositions were established and the total dissociation constants of complex oxalate ions of Pu (III) were calculated by the method of least squares. Within the range of $\text{K}_2\text{C}_2\text{O}_4$ concentrations studied, the following complex ions are formed (more precisely, the relationship between Pu (III) and $\text{C}_2\text{O}_4^{2-}$ ions):



the total concentration dissociation constants of which are, respectively, $4.9 \cdot 10^{-10}$, $4.1 \cdot 10^{-10}$ and $1.2 \cdot 10^{-10}$. The dependence of the concentration of these ions on the concentration of complex-former is shown in Fig. 1.

The solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in aqueous solutions of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in the region of ammonium oxalate concentrations of 0.07 to 0.7 mole/liter (see Table 1) were similarly determined. It was established that, under these conditions, complex ions having the same compositions are formed, the total dissociation constants of which are $[\text{Pu}(\text{C}_2\text{O}_4)_2]^- 11.6 \cdot 10^{-9}$, $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{3-} 5.6 \cdot 10^{-9}$, $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{5-} 2.5 \cdot 10^{-9}$.

The heat of formation of the complex ions was also calculated for the reaction: $\text{Pu}^{3+} + n\text{C}_2\text{O}_4^{2-} \rightleftharpoons [\text{Pu}(\text{C}_2\text{O}_4)_n]^{3-2n}$ (1). It was found that ΔQ for the ion $[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$ is 1300 cal, for $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{3-}$ it is 1200 cal, and for $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{5-}$ it is 1300 cal.

The data on complex formation of Pu (III) with the $\text{C}_2\text{O}_4^{2-}$ ion obtained by the solubility method were confirmed by the ion-exchange method.

* The solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in water is $4.32 \cdot 10^{-6}$ mole/liter at 20° and $1.88 \cdot 10^{-6}$ mole/liter at 70°.

The variation in the distribution of Pu (III) between a one molar solution of NH_4Cl and KU-2 cation exchange resin with the pH of the solution was investigated. NH_4Cl was added to maintain constant ionic strength of the solutions ($\mu \approx 1$).

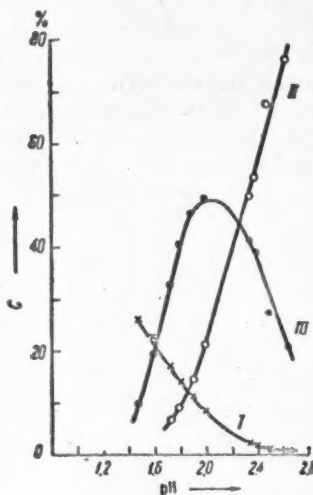


Fig. 2. Effect of pH of the solution on the concentration of the ions: I) Pu^{3+} , II) $[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$, III) $[\text{Pu}(\text{HC}_2\text{O}_4)_4]^-$.

$[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$, are formed, the total dissociation constants of which are, respectively, $1.1 \cdot 10^{-11}$ and $7.1 \cdot 10^{-10}$. In Fig. 2 is shown the relationship between the concentrations of the complex ions $[\text{Pu}(\text{HC}_2\text{O}_4)_4]^-$ and $[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$ and also of free Pu^{3+} ions and the pH of the solution.

The distribution of Pu (III) between a 1 M solution of NH_4Cl and the cation exchange resin was also studied in the presence of 0.005 M $\text{H}_2\text{C}_2\text{O}_4$ with a variation in the pH of the solution from 1.4 to 3.0. The solutions containing the adsorbent ($v = 25$ ml; weight of resin sample 0.5 g) were agitated for 3 hours in an atmosphere of nitrogen at a temperature of $20 \pm 1^\circ$ until equilibrium was established (the experiments were carried out with indicator amounts of plutonium). The experimental data are shown in Table 2.

In the pH interval investigated, 1.4-3.0, both $\text{C}_2\text{O}_4^{2-}$ ions and HC_2O_4^- ions were able to take part in complex formation. The concentrations of these ions were determined from the equations for the first and second stages of dissociation of oxalic acid at an ionic strength, created by NaCl , of $\mu \approx 1$. The dissociation constants of $\text{H}_2\text{C}_2\text{O}_4$, determined by us by potentiometric titration, are:

$$K_1 = 1.4 \cdot 10^{-2} \quad \text{and} \quad K_2 = 1.5 \cdot 10^{-4}.$$

Calculations by the method of Shubert et al [9] showed that, in these solutions in the pH interval of 1.4-3.0, the complex ions $[\text{Pu}(\text{HC}_2\text{O}_4)_4]^-$ and

TABLE 2

Distribution of Pu (III) Between a 1 M Solution of NH_4Cl and the Cation Exchange Resin at Various pH Values

In absence of complex former				In presence of complex former		
equilibrium pH of NH_4Cl solution	concn. of Pu^{3+} in equil. sol. % of init. a_0	amount of Pu^{3+} absorbed % of init. q_0	$A = \frac{a_0}{q_0}$	equilibrium pH of solution	total amt. of Pu^{3+} in equil. sol. % of init. a	amount Pu^{3+} absorbed % of init. q
1.63	28.4	71.6	0.40	1.47	35.8	64.2
2.00	28.6	71.4	0.40			
2.29	28.5	71.5	0.40	1.60	42.6	57.4
2.40	27.8	72.2	0.39	1.73	56.8	43.2
2.95	29.0	71.0	0.41	1.80	64.4	35.6
3.18	30.6	69.4	0.44	1.90	72.3	27.7
3.34	27.4	72.6	0.38	2.00	79.0	21.0
3.48	29.1	70.9	0.41	2.35	94.0	6.0
				2.40	95.0	5.0
				2.50	96.8	3.2
				2.65	98.0	2.0

The value of the total dissociation constant of the complex ion $[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$ obtained by the ion exchange method agrees satisfactorily with the value obtained by the solubility method.

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• In Russian.

FERROCENE HOMOLOGS WITH TERTIARY ALKYL RADICALS

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The alkylation of ferrocene by the Friedel-Crafts reaction, carried out by us for the first time [1, 2], gave a series of C_1 to C_5 monoalkyl homologs of ferrocene as well as dialkylferrocenes and some polyalkylated homologs. From the infrared spectra [2, 4] it was established that the thus obtained dialkylferrocenes contained both alkyl groups on one ring of the dicyclopentadiene.

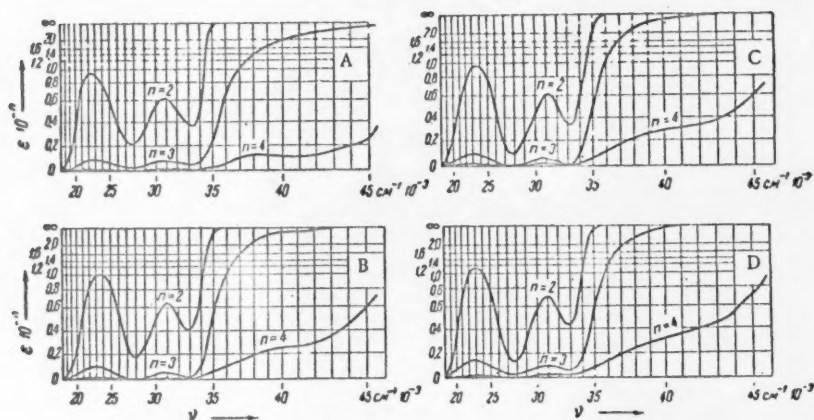


Fig. 1. Ultraviolet absorption spectra of ferrocene (A), ethylferrocene (B), isopropyl ferrocene (C), and tert-butylferrocene (D). Solvent - isooctane; $C_{mol} = 1 \cdot 10^{-4}$; $d = 0.5$ cm.

In the present work, we were able to use isobutylene as the alkylating agent, in addition to alkyl halides, and to obtain up to 50% mono-tert-butylferrocene with an over-all yield of alkylation products of 30% depending on the conditions selected (see Table 2). Tert-butylferrocene, di-tert-butylferrocene, and di-tert-amylferrocene, just as in the case of all alkylation products previously prepared by us, contain one free ring in the dicyclopentadiene nucleus and have characteristic frequencies in the regions of 1003 and 1107 cm^{-1} . A comparison of the experimental values of the molecular refraction shows that the usual additivity of molecular refraction occurs in the alkylferrocene series (see Table 1); this agrees with the almost complete identity of the absorption curves in the ultraviolet region of ferrocene itself and its homologs* (see Fig. 1).

* Measurement of the u. v. spectra was carried out by I. Ya. Kachkurova in the Laboratory of the Corresponding Member of the Academy of Sciences, USSR, I. V. Obrel'mov, for which the authors express their deep appreciation.

The difference between the experimental molecular refractions and the total of the C and H atomic refractions in the ferrocene homologs investigated by us varied from 13.58 to 13.89 and averaged 13.74. This difference includes the atomic refraction of iron and the structural increment for ferrocene (π -bonds, etc.), and can be provisionally called the ferrocene increment. This value leads to a calculated molecular refraction for ferrocene of 48.91, and not 46.8 (as given in the paper by Richmond and Freiser [3] with reference to the communication of Woodward). It is impossible to say how well this value retains its constancy in other ferrocene derivatives.

TABLE 1

	n_D^{20}	d_4^{20}	M	MR_{found}	Sum of C and H atomic refractions*	Ferrocene increment incl. atomic refraction for iron	Homologous difference per CH_2 *	
							found	calc.
$\text{C}_2\text{H}_5\text{C}_{10}\text{H}_9\text{Fe}$ (?)	1.6016	1.2628	244.08	58.06	44.316	13.74	—	—
$(\text{C}_2\text{H}_5)_2\text{C}_{10}\text{H}_8\text{FeI}$ (?)	1.5822	1.2002	242.13	67.35	54.652	13.70	4.64	4.618
$(\text{C}_2\text{H}_5)_3\text{C}_{10}\text{H}_7\text{FeII}$ (?)	1.5850	1.2041	242.13	67.39	53.652	13.74	4.66	4.618
$i\text{-C}_3\text{H}_7\text{C}_{10}\text{H}_9\text{Fe}$	1.5897	1.2230	228.11	62.92	49.034	13.89	4.86	4.618
$t\text{-C}_4\text{H}_9\text{C}_{10}\text{H}_9\text{Fe}$	1.5790	1.2013	242.13	67.54	53.652	13.89	4.62	4.618
$t\text{-C}_5\text{H}_{11}\text{C}_{10}\text{H}_9\text{Fe}$	1.5760	1.1798	256.16	71.85	58.270	13.58	4.31	4.618
Average						13.74	4.62	

* Atomic refractions according to Eisenlohr.

EXPERIMENTAL METHODS

Tert-butylferrocene from ferrocene and tert-butyl chloride. A solution of 7.5 g of tert-butyl chloride in 20 ml of absolute petroleum ether was introduced over the course of an hour into a solution of 40 g of ferrocene in 300 ml of absolute petroleum ether. After heating for 5 hours at 50°, decomposition of the reaction mixture was carried out by the usual method [1]. 17 g of ferrocene (m. p. 172-173°) was recovered; 14.8 g of liquid reaction products was obtained. 5.3 g of tert-butylferrocene was obtained; $n_D^{20} = 1.5790$; $d_4^{20} = 1.2013$; b. p. 103-105°/4 mm. $MR_{\text{found}} = 67.54$.

Found %: C 69.54, 69.46; H 7.42, 7.50; Fe 22.90, 22.98. $\text{C}_{14}\text{H}_{18}\text{Fe}$. Calculated %: C 69.51; H 7.40; Fe 23.09.

6.8 g of di-tert-butylferrocene was also obtained; $n_D^{20} = 1.5581$, $d_4^{20} = 1.1336$, b. p. 124.5-125°/3 mm. $MR_{\text{found}} = 85.51$.

Found %: C 72.56, 72.40; H 8.46, 8.42; Fe 19.04, 18.73. $\text{C}_{18}\text{H}_{26}\text{Fe}$. Calculated %: C 72.98; H 8.69; Fe 18.43.

In addition, a high-boiling fraction, b. p. 130-180°/4 mm, was also obtained; this fraction was not investigated further. According to the analytical results, the polyalkylation products contained an average of 4 butyl radicals per ferrocene group.

Found %: C 76.67, 76.55; H 8.96, 9.00; Fe 13.75, 13.58. $\text{C}_{26}\text{H}_{42}\text{Fe}$. Calculated %: C 76.25; H 10.10; Fe 13.65.

Tert-butylferrocenes from isobutylene. A suspension of 20 g of ferrocene, 200 ml of absolute n-heptane, and varying amounts of cooled, liquid isobutylene and dry aluminum chloride (see Table 2) were charged to a steel autoclave of 0.5 liter volume and heated with continuous agitation for various times. After decomposition by the usual method and distillation of the solvent, a certain amount of ferrocene was recovered and liquid products of a dark red color were obtained (see Table 2).

TABLE 2

Amount of reactants			Reaction temperature, °C	Time, hours	Ferrocene recovered, g	Liquid products obtained, g	Average yield, % of reacted ferrocene	Fraction I 100-110°/5 mm, n_D^{20} = 1.5760 - 1.5790		Fraction II 110-120°/5 mm, n_D^{20} = 1.5550 - 1.5580		Fraction III above 130°/5 mm $n_D^{20} \approx 1.54$	
Ferrocene, g	$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_3$, ml	AlCl_3 , g						g	% of over-all yield	g	% of over-all yield	g	% of over-all yield
20	30	—	50-60	5	16	0.8	2	0.15	18.8	0.07	8.7	0.16	20
20	30	0.5	50-60	5	6.8	2	5	0.16	8	0.2	10	0.48	24
20	30	1.0	50-60	5	11.4	1.6	4	0.22	13.7	0.32	20	—	—
20	30	7.5	50-60	5	—	31	—	—	—	—	—	7.3*	20**
20	30	7.5	20	24	8	6.3	30	3.2	51	2.35	37.3	—	—
20	250	7.5	20	24	—	92	100	—	—	—	—	12*	40**

* And higher-boiling products.

** Yield calculated in percent of ferrocene used.

Tert-amylferrocenes from 2-methyl-2-chlorobutane. Similarly, from 40 g of ferrocene and 30 ml of 2-methyl-2-chlorobutane, was obtained 1.9 g (13.7%) of tert-amylferrocene, $n_D^{20} = 1.5760$, $d_4^{20} = 1.1798$. M_R found = 71.85, b. p. 135-136°/4 mm.

Found %: C 70.44, 70.40; H 7.85, 7.87; Fe 21.69, 21.51. $\text{C}_{15}\text{H}_{20}\text{Fe}$. Calculated %: C 70.327; H 7.870; Fe 21.813.

The yield of di-tert-amylferrocene was 2.6 g (15.2%), $n_D^{20} = 1.5602$, $d_4^{20} = 1.1469$; b. p. 162-163° per 4 mm.

Found %: C 73.95, 73.65; H 8.86, 8.73; Fe 18.37, 16.80. $\text{C}_{20}\text{H}_{30}\text{Fe}$. Calculated %: C 73.61; H 9.267; Fe 17.123.

30 g of unreacted ferrocene was recovered.

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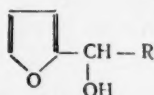
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SELECTIVE REDUCTION OF ALKYL-FURYL-CARBINOLS TO ALKYL-FURANS OVER PALLADIUM CATALYST

Corresponding Member AN SSSR N. I. Shuikin and I. F. Belsky

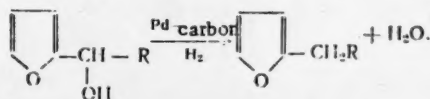
Hydrogenation reactions of compounds of the type



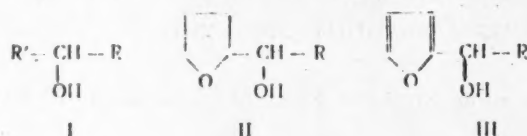
where R is a hydrogen atom or an alkyl or aryl radical, have been studied in considerable detail both with respect to diversity of compounds and with respect to the number of catalysts used. Depending on the nature of the catalyst and the structure of the compound, hydrogenation of the latter can proceed in three directions: 1) only the double bond in the furan ring undergoes hydrogenation, which results in the preparation of alcohols of the tetrahydrofuran series; 2) hydrogenolysis of the ring can occur at one or both C-O bonds with the formation of the corresponding alkanediols and alkanols; 3) complete reduction of the substituent group can occur with replacement of the hydroxyl by an atom of hydrogen; 4) finally, all or some of the indicated reactions can proceed simultaneously under specific conditions.

Nickel catalysts, Raney nickel in particular, are very active in promoting the hydrogenation of the multiple bonds in the furan ring. Thus, Paul [1] obtained the corresponding derivatives of tetrahydrofuran in yields of 90-100% by the hydrogenation of furfuryl alcohol and of methyl-, ethyl-, propyl-, and phenylfuryl-carbinols over Raney nickel at 50-80°. Over a platinum catalyst promoted with iron salts, hydrogenation of furfuryl alcohol [2] and of alkylfurylcarbinols [3] also proceeded chiefly with the formation of the corresponding tetrahydro derivatives. However, this catalyst, even at low temperatures, promotes hydrogenolysis of the furan ring at one or the other of the ether bonds, which results in the formation of alkanediols and alkanols. This latter reaction proceeds especially readily over copper catalysts, particularly copper chromite. Connor and Adkins [4] obtained sylvan, 1-pentanol, and 1,2- and 1,5-pentanediois as a result of the hydrogenation of furfuryl alcohol over copper chromite in the liquid phase at 200-250°. Copper catalysts in a different form have been shown to be most effective in the reduction of the hydroxyl group in furfuryl alcohol without hydrogenation of the double bonds in the ring [5]. This reaction has found industrial application in the production of sylvan from furfural.

As is well known, palladium is an excellent catalyst for the hydrogenation of the double bonds in the furan ring both in the liquid [6] and in the vapor [7] phase. However, attempts undertaken by us to hydrogenate the furan ring in alkylfurylcarbinols in the vapor phase over palladinized carbon led to unexpected and interesting results. Instead of hydrogenation of the double bonds in the furan ring, hydrogenolysis of the C-OH bond and replacement of the hydroxyl group by a hydrogen atom occurred. This led to the conversion of methyl- and ethylfurylcarbinols, respectively, to α -ethyl- and α -propylfuran in yields of 70-80% of theoretical:

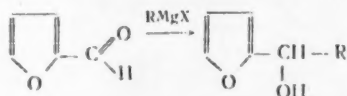


The ability of the bond between the carbon atom and the hydroxyl group in alkylfurylcarbinols readily to undergo cleavage under the influence of hydrogen and in the presence of catalysts is a specific property of this type of compound. Thus, the hydroxyl group in 2-pentanol is not replaced by hydrogen in any appreciable amount, even at higher temperatures. It is a very significant fact that the hydroxyl group in alkyltetrahydrofurylcarbinols has absolutely no tendency toward reduction under those conditions under which this reaction occurs with alkylfurylcarbinols. Methyltetrahydrofurylcarbinol remained unchanged when we passed it over palladinized carbon under the same conditions under which the hydrogenation of methylfurylcarbinol took place. Thus, of the three types of compounds



only in the alkylfurylcarbinols (III) was the C-O bond in the side chain so greatly weakened that it cleaved readily under the influence of hydrogen in the presence of palladinized carbon. The reason for this fact must apparently be sought in the effect of the conjugation of the C-O bond in the side chain with the double bond in the furan ring.

The methyl- and ethylfurylcarbinols were synthesized according to the scheme:



The methylfurylcarbinol had the following properties: b. p. 76-77° (23 mm), d_4^{20} 1.0780 and n_D^{20} 1.4800.

The ethylfurylcarbinol boiled at 73-75° (8 mm) and had d_4^{20} 1.0492 and n_D^{20} 1.4786.

The methyltetrahydrofurylcarbinol, prepared by the hydrogenation of methylfurylcarbinol in the liquid phase over skeletal Ni-Al catalyst at 130-150° had the following constants: b. p. 92-93°/40 mm, d_4^{20} 1.0150, n_D^{20} 1.4485.

The palladinized carbon was prepared by the method of Zelinsky [8] — impregnation of activated birchwood charcoal with a solution of H_2PdCl_4 and subsequent precipitation of finely dispersed palladium on the carbon by means of formalin and potassium hydroxide solution. The difference in the methods of preparation of our catalyst and the catalyst of Zelinsky is that in the preparation of our catalyst precipitation of the Pd black on the carrier in the presence of formalin was carried out by means of potassium hydroxide rather than sodium hydroxide, the former, according to the observations of one of us, being a promoter of metallic catalysts. Moreover, after precipitation of the Pd black on the carbon, we removed the excess alkali with dilute hydrochloric acid, and not acetic acid. This method eliminated the formation of a colloidal film and guaranteed preparation of a catalyst with reproducible properties.

Hydrogenation of 50 g portions of the alkylfurylcarbinols was carried out in the vapor phase at 200-230° at a space rate of 0.1 hour⁻¹. The catalyzates were dried with calcium chloride and distilled in a column equivalent to 40 theoretical plates.

The α -ethylfuran and α -propylfuran which were obtained in yields of 80 and 70% of theoretical, respectively, had the following properties:

α -Ethylfuran: b. p. 91-91.5°/750 mm, d_4^{20} 0.9018 and n_D^{20} 1.4402.

α -Propylfuran: b. p. 114-115°/750 mm, d_4^{20} 0.8876 and n_D^{20} 1.4395.

The reductive dehydroxylation of alkylfurylcarbinols is a very interesting case of selective action of a palladium catalyst. Apart from theoretical interest, it could be important as a method of preparation, since, in the synthesis of alkylfurans, it permits elimination of the step of dehydrating alkylfurylcarbinols, which does not usually proceed very smoothly.

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ON THE PROBLEM OF THE PREPARATION OF TRIVALENT NEPTUNIUM

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In papers devoted to the chemistry of neptunium, comparatively little space has been allotted to the trivalent state of this element. This can be explained by the difficulty in preparing and investigating Np (III). Np (III) oxidizes rapidly in air, particularly in the presence of fluorides or oxalates and also in alkaline media [1]. Dilute solutions of Np (III) (0.005 M) in 1 M HCl have a pale violet color and are similar in appearance

to solutions of U (III) and Pu (III) [2]. The absorption spectra of Np (III) in perchloric [3] and hydrochloric acid [4] solutions have been measured and the molar absorption coefficients have been calculated for the various maxima, the chief of which are at wave lengths of 402, 416, 462, 553, 602, 661, and 788 m μ .

Up to the present, electrochemical methods [3, 4] have been used for the preparation of Np (III), considerable precaution being required to retain the neptunium in the trivalent state.

The aim of our work was to investigate the possibility of preparing Np (III) by a chemical route, specifically by the action of rongalite (formaldehyde - sodium sulfoxylate, $\text{NaHSO}_2 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$) on a solution of neptunium. Determination of the valence states of the neptunium in the solutions was carried out by the spectrographic method using an SF-4 apparatus. The standard of comparison used in all of the measurements was a solution containing the same components as the solution being measured (with the exception of neptunium) and subjected to the same operations.

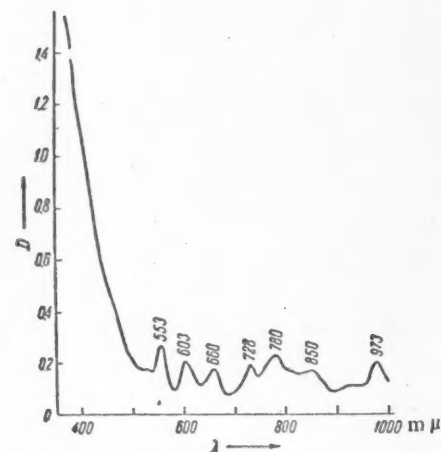


Fig. 1. Absorption curve of a solution of neptunium (1 M HNO_3 ; $(\text{NH}_4)_2\text{SO}_4$ 10 g/liter) reduced with rongalite in an atmosphere of nitrogen.

The action of rongalite on nitric acid solutions of neptunium. The addition of rongalite to a cell containing a solution of neptunium (IV) in 1.3 M HNO_3 led to a change in the color from yellow-green to an intense yellow. A change in the absorption spectrum disclosed the formation of neptunium (III) in the solution.

The presence in the absorption spectrum of the reduced neptunium solution of maxima at wavelengths of 659, 784, and 850 m μ indicated reduction of the neptunium to the trivalent state. The most complete reduction was reached after 30-45 minutes.

In the majority of the experiments, the concentration of the rongalite comprised 10 g/liter and that of neptunium was 1-1.5 g/liter. The experiments on the reduction of neptunium were carried out in an atmosphere of nitrogen in order to protect the neptunium (III) solution from oxidation by atmospheric oxygen.

A certain amount of Np (IV) remained in the solution, as may be seen from the maxima at 728 and 973 m μ (Fig. 1). However, the stability of Np (III) was appreciably increased; there was no change in the spectrum of a solution which had stood in a covered cell for a day, indicating no oxidation. On purging with air, the neptunium was again converted to the tetravalent state. Taking the content of neptunium (IV) in the oxidized solution as 100% from the height of the maxima at 728 and 973 m μ it was determined that reduction by rongalite proceeded to the extent of approximately 70%.

The action of rongalite on hydrochloric acid solutions of neptunium. The addition of rongalite to a hydrochloric acid solution of neptunium (IV) led to its reduction to the trivalent state. The most complete reduction was reached 30-60 minutes after the addition of the rongalite. However, while in nitric acid solutions an increase in the absorption maxima of Np (IV) was observed after the solutions had stood 2 hours in air, insignificant oxidation was observed in hydrochloric acid solution after 4 hours. The hydrochloric acid solution had a violet-blue color.

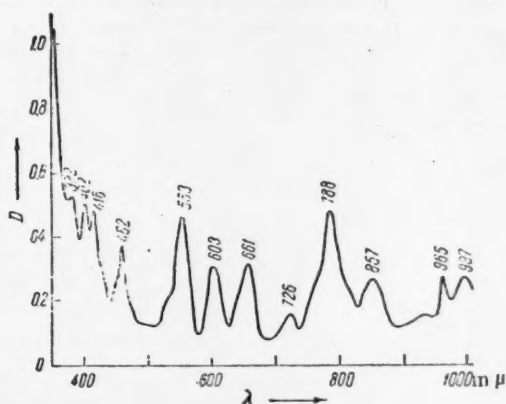


Fig. 2. Absorption curve of a solution of Np (III) containing some (IV) in 1 M HCl.

As in the case of the nitric acid solutions, in order to determine the completeness of reduction we took the content of neptunium (IV) in an oxidized solution as 100%. A calibration curve was constructed showing the variation in the height of the maximum at 728 m μ with the content of Np (IV). Using this curve, it was determined that reduction of neptunium to the trivalent state in hydrochloric acid solutions containing no other reducing agents proceeded to the extent of 75-78%. In the presence of hydrazine ($N_2H_4 \cdot HCl$, 20 g/liter), the reduction increased to 84-86%. Carrying out the process in an atmosphere of nitrogen increased reduction to 90-94%. After standing for a day in an atmosphere of nitrogen, no sign of oxidation was observed (Fig. 2).

Thus, more complete reduction to Np (III) proceeds in hydrochloric acid solutions, and the Np (III) is more stable than in nitric acid solutions.

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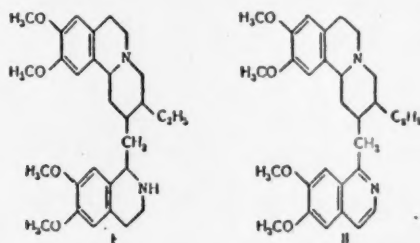
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SYNTHESIS OF THE ALKALOID EMETAMINE

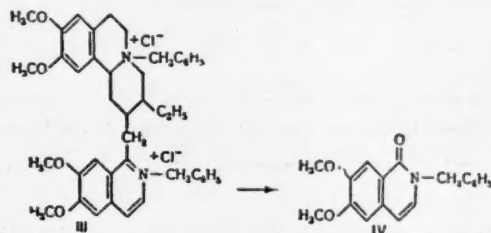
R. P. Evstigneeva, Yu. Braier, and N. A. Preobrazhensky

(Presented by Academician I. N. Nazarov, June 27, 1957)

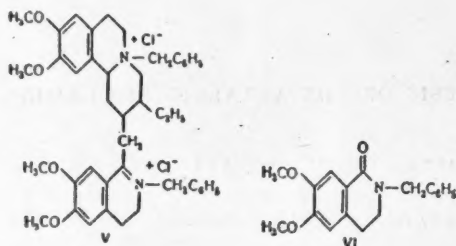
Emetamine is a representative of the group of alkaloids isolated from the roots of ipecacuanha. It is present in the plant in very small amount, and is very difficult to isolate in the pure form. It has been established that it differs from the major alkaloid of ipecacuanha — emetine — in that it contains less hydrogen (4 atoms). It has been proposed that the emetamine structure contains an isoquinoline ring, while emetine is a derivative of tetrahydroisoquinoline [1]. The fundamental conversions of the alkaloid confirmed this possibility. However, the structure proposed at that time was based on an incorrect structure for emetine. After establishing the structure of emetine (I), structure II was assumed for emetamine.



That structure II is correct was recently confirmed by conversion of the bisbenzyl chloride of emetamine (III) to N-benzylisoquinoline (IV) by permanganate oxidation [2].

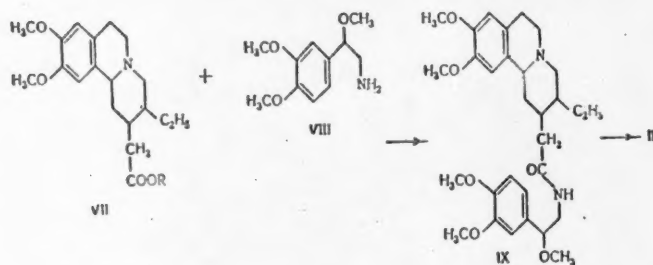


On the basis of similar conversions of the bisbenzyl chloride of *o*-methylpictotrine (V), which led to the preparation (in good yield) of benzylcorydaldine (VI), it can be assumed that the double bond of isoquinoline derivative IV could not have been formed by oxidation.



The present communication describes the synthesis of racemic emetamine, as a result of which the structure of this alkaloid can be considered as definitely established.

The synthesis was carried out by the route previously developed by us for the preparation of emetine [3].



The methyl ester of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenz-(1,2:1',2')-quinolizyl-7-acetic acid (VII) was obtained by the method previously described by us [3] using skeletal nickel catalyst for the reduction of the quaternary chloride. The melting point of the hydrochloride (crystal hydrate) was 195-195.5° (sinters 189°). β -(3,4-Dimethoxyphenyl)- β -methoxyethylamine (VIII) was obtained from vanillin [4]. B. p. 112-115° per 1 mm.

By heating ester VII with amine VIII at 180-200° in a stream of nitrogen, amide IX was obtained; it separated from anhydrous ethyl alcohol in the form of colorless crystals. M. p. 172.5-173.5°.

Found % C 68.66, 68.45; H 7.97, 7.83; N 5.49, 5.48. $C_{30}H_{42}O_6N_2$. Calculated % C 68.44; H 8.02; N 5.31.

Cyclization of the amide by means of phosphorus oxychloride in toluene led to emetamine. The base was isolated in the form of a white amorphous material which was converted to the oxalate.

M. p. 141.5-142.5° (from ethyl alcohol). Prior to analysis, the preparation was dried at 117° and 1 mm for an hour.

Found % C 60.23, 60.64; H 6.16, 6.12; N 3.89, 3.84. $C_{29}H_{36}O_4N_2 \cdot 2C_2H_2O_4$. Calculated %: C 60.34; H 6.14; N 4.27.

The emetamine base, liberated from the oxalate had a melting point of 124-125° (sinters 70°).

Found %: C 73.46; H 7.58; N 5.55. $C_{29}H_{36}O_4N_2$. Calculated %: C 73.10; H 7.62; N 5.88.

Oxidation of the racemic base of enetamine with bromine gave rubremetamine bromide in the form of orange-red crystals, M. p. 170-185°.

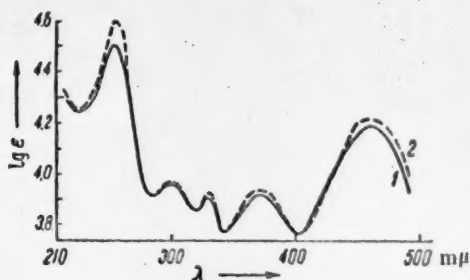


Fig. 1. Ultraviolet absorption spectra in water:
1) synthetic rubremetamine bromide, 2) rubremetamine
bromide from the natural alkaloid [5].

The ultraviolet absorption spectrum of the synthetic rubremetamine bromide was identical with the spectrum of rubremetamine bromide obtained from the natural alkaloid [5] (Fig. 1).

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**ON THE DIAZOTIZATION OF 2-p-AMINOARYLINDONES.
PREPARATION OF AZO DYES CONTAINING AN INDENE RING**

Ch. P. Ivanov and B. V. Aleksiev

(Presented by Academician I. N. Nazarov, June 27, 1957)

In previous work, it was established that nitro derivatives of 2,3-diaryl- and 2-aryl-3-alkylindones, reported by us in reference [1], are converted with high yield to the corresponding aminoindone by the action of ferrous sulfate in alkaline medium [2]. The aim of the present work was to establish suitable conditions for the diazotization of aminoindones thereby permitting preparation of azo dyes containing an indone ring, which have not been obtained up to the present time. Only certain azo dyes containing a hydrindone ring have been described in the literature [3, 4].

The usual methods of diazotization cannot be used for aminoindones owing to their weakly acidic nature and to the poor solubility of their salts in water. We first attempted to carry out the diazotization in acetic acid medium [5] and to couple the probably resulting diazonium salt with β -naphthol. However, a dark brown, oily product was obtained, which was not investigated further. Experiments on diazotization in a medium of concentrated sulfuric acid in the presence of phosphoric acid [6] and coupling with β -naphthol were also unsuccessful. Then, we attempted to carry out the diazotization of aminoindones in not quite concentrated sulfuric acid medium, using a solvent with a basic nature according to de Milt and van Zandt [7], and to couple the resulting diazonium salt with β -naphthol. From the neutral ethereal solution we isolated a dark red-violet mass with a m. p. of 197-199°, difficultly soluble in alcohol and insoluble in water and alkalis. Having in mind that β -naphthol always couples in the α -position, thereby yielding products which are insoluble in alkalis and difficultly soluble in organic solvents [8], and considering the results of a determination of the nitrogen content of this compound, we consider that it is a benzeneazonaphthol containing an indone ring, namely, p-(2-(3-phenylindonyl))benzeneazo-1-(2-naphthol) (see Table 1). From the alkaline extract obtained in this same experiment, we isolated, along with unreacted β -naphthol, a small amount of red crystals with a m. p. of 281-285.5°, soluble in dilute alkali in the cold and insoluble in water. Our supposition that this product was 2-p-hydroxyphenyl-3-phenylindone, described by Koelsch [9], was not confirmed. It was found that these crystals contain a considerable percentage of nitrogen, an amount corresponding to that calculated for the corresponding diazoic acid of diphenylindone (X). It is well known that some anti-forms of diazoic acids possess considerable stability, in which connection a similar structure of the product can be considered probable. We obtained the above-described 2-p-hydroxyphenyl-3-phenylindone by decomposition of the diazonium salt of aminodiphenylindone under previously described conditions [10] but at 75-80°.

In order to obtain water-soluble compounds, we attempted to couple diazotized aminodiphenylindone with R-salt and H-acid. Coupling with R-salt was carried out in soda solution. After salting out with sodium chloride at 70°, a dark red crystalline powder was obtained which was soluble in water. It dyed wool and silk a dark red color. The dye had a fastness of 5 on wool (fastness to washing and perspiration was determined). The method of preparation, the properties, and the results of a determination of nitrogen content of this product provided basis for the assumption that it is the disodium salt of p-(2-(3-phenylindonyl))-benzeneazo-1-(2-naphthol)-3,6-disulfonic acid (IV).

Coupling with H-acid was first carried out in a mineral acid medium at a pH of about 2-2.5. A dark blue-violet crystalline powder, which colored wool and silk violet-red, was obtained. Fastness of the dye on wool was 5 (to washing and perspiration). Having in mind that H-acid couples with diazonium salts in mineral acid medium in the 7-position, we consider that this compound is the disodium salt of p-(2-(3-phenylindonyl))-benzeneazo-7-(8-amino)-(1-naphthol)-3,6-disulfonic acid (VII). Coupling of diazotized aminodiphenylindone with H-acid in alkaline medium was also carried out. This gave a dark violet crystalline powder which was readily soluble in water and which imparted a black color with a violet tint to wool and silk. From the above considerations, we assume that this compound is the disodium salt of p-(2-(3-phenylindonyl))-benzeneazo-2-(8-amino)-(1-naphthol)-3,6-disulfonic acid (XI).

TABLE 1

Compound	Ar(R)	X	M.p. °C	Yield, %	N calc. %	N, found (by Kjeldahl), %
I	C ₆ H ₅		197-199	52.7	6.19	6.03; 6.00
II	C ₆ H ₄ ·CH ₂ -n		226-228	46.0	6.0	5.71; 5.76
III	C ₆ H ₅		187.5-189	48.4	6.93	6.91; 7.10
IV	C ₆ H ₅		—	80.2	4.27	4.34; 4.28
V	C ₆ H ₄ ·CH ₂ -n		—	80.7	4.18	4.21; 4.14
VI	C ₆ H ₅		—	70.0	4.60	4.55; 4.67
VII	C ₆ H ₅		—	79.5	6.26	5.99; 6.06
VIII	C ₆ H ₄ ·CH ₂ -n		—	76.8	6.13	5.89; 5.90
IX	C ₆ H ₅		—	67.7	6.74	6.54; 6.48
X	C ₆ H ₅		281-282.5	—	8.50	8.63; —

From diazotized aminodiphenylindone and H-acid was obtained the corresponding primary disazo dye by successive coupling in mineral acid and alkaline medium. It was a black, crystalline powder for which we assume the structure of the disodium salt of bis(p-(2-(3-phenylindonyl))benzeneazo-2,7-(8-amino)-1-naphthol 3,6-disulfonic acid (XII). This product imparted a black color with a dark blue tint to wool and silk. At concentrations of less than 1%, it colored wool gray.

The diazotization of 2-p-aminophenyl-3-p-tolylindone proceeded similarly. Coupling the diazonium salt with 8-naphthol gave p-(2-(3-p-tolylindonyl))-benzeneazo-1-(2-naphthol) (II), which had properties similar to I. On coupling with R-salt and H-acid, products similar to those described above were obtained, for which we assume the structures of the disodium salts of p-(2-(3-p-tolylindonyl)) benzeneazo-1-(2-naphthol)-3,6-disulfonic acid (V) and p-(2-(3-p-tolylindonyl)) benzeneazo-7-(8-amino)-(1-naphthol)-3,6-disulfonic acid (VIII).

The disodium salt of 2-p-aminophenyl-3-ethylindone was obtained by a similar method. On coupling with β -naphthol, it gave p-(2-(3-ethylindonyl)) benzeneazo-1-(2-naphthol) (III), and with R-salt and II-acid it gave the disodium salts of, respectively, p-(2-(3-ethylindonyl)) benzeneazo-1-(2-naphthol)-3,6-disulfonic acid (VI) and p-(2-(3-ethylindonyl)) benzeneazo-7-(8-amino)-(1-naphthol)-3,6-disulfonic acid (IX).

EXPERIMENTAL RESULTS

1. Coupling of aminoindones with β -naphthol. 0.310-0.414 g (0.0015 mole in 3-4 fold excess) of powdered sodium nitrite was dissolved in a mixture of 14 ml of concentrated sulfuric acid and 7 ml of water while heating to 70°. After cooling to 10°, a solution of 0.446 g (0.0015 mole) of aminodiphenylindone in 10 ml of pyridine was added dropwise with continuous vigorous stirring. The temperature must not rise above 10° during the addition. After stirring for an hour, the mixture was diluted with twice its volume (62 ml) of ice water, and 2 g of urea was added. To the resulting, almost transparent, orange-red solution was added, at the same temperature, a solution of 0.227 g (0.0015 mole \pm 5% excess) of β -naphthol in 10 ml of pyridine and the resulting mixture was alkalinized with dilute alkali solution. After an hour, the mixture was acidified with dilute sulfuric acid and extracted with ether. The violet-red ethereal solution was successively treated with 18% hydrochloric acid and dilute alkali. After distillation of the ether, 0.358 g of dark red-violet crystals with a m. p. of 197-199° (from alcohol) (I) was obtained from the neutral solution. The crystals were insoluble in water and alkali, slightly soluble in alcohol, and very soluble in benzene and acetone. From the alkaline extract, after acidification and extraction with ether, was obtained 0.270 g of acidic products, from which, after washing with 10 ml of ether, was isolated 0.021 g of red crystals with a m. p. of 281-282.5° (X). 0.039 g of products with a basic nature was separated from the acid extract.

In a similar manner, 0.322 g of violet-red crystals with a m. p. of 226-228° (from alcohol) (II) was obtained from 0.467 g of aminophenyltolylindone. 0.204 g of acidic and 0.115 g of basic products were isolated from the alkali and acid extracts, respectively, in this case. By treatment of the acidic products with 10 ml of ether, 0.018 g of brick red crystals with a m. p. of 284-286° was isolated. In a similar manner, from 0.450 g of aminophenylethylindone was obtained 0.353 g of reddish brown crystals with a m. p. of 187.5-189° (from alcohol) (III). In this case, 0.280 g of acidic and 0.055 g of basic products were obtained. From the extracted alkaline product was obtained 0.015 g of brown crystals with a m. p. of 275-276.5°.

2. Coupling of aminoindones with R-salt. 0.653 g (0.0015 mole and 25% excess) of R-salt was dissolved in 150-200 ml of a concentrated solution of sodium carbonate, the solution was cooled to 2-5°, and to the solution was added dropwise a solution of 0.446 g of aminodiphenylindone which had been diazotized by the above-described method. The resulting dye was separated by salting out with sodium chloride (16-17 g per 100 ml of solution) at 70° (sp. gr. of filtrate 1.17-1.18 at 20°), washed with a sodium chloride solution of 1.17 sp. gr., dissolved in water, and salted out and filtered again under the same conditions. After drying at 100°, the dye was extracted by repeated boiling with absolute alcohol. After concentration to a small volume, there was obtained 0.790 g of a dark red crystalline powder (IV) which was readily soluble in water, slightly soluble in alcohol, and insoluble in benzene and ether. In similar experiments, from 0.234 g of aminophenyltolylindone was obtained 0.405 g of a red crystalline powder (V) and from 0.225 g of aminophenylethylindone was obtained 0.388 g of a brick red powder (VI) with properties similar to those described above.

3. Coupling of aminoindones with II-acid. 0.446 g of aminodiphenylindone was diazotized by the method described above, diluted with ice water, and to the solution was added 2 g of urea. Then, at a temperature of 2-5° and with intense stirring, a solution of 0.640 g (0.0015 mole and 25% excess) of II-acid in 30 ml of water was added dropwise. The pH of the medium was reduced to 2-2.5 by means of an aqueous

solution of sodium acetate, and the mixture was stirred another 5-6 hours at this same temperature, during which it was necessary to have an excess of H-acid (tested with benzenediazonium chloride) in the solution. The resulting dye was separated and purified by the method described above, which gave 0.802 g of a dark blue-violet powder (VII), similar to IV in properties. Under the same conditions, from 0.234 g of aminophenyltolylindone was obtained 0.395 g of a violet-blue crystalline powder (VIII). Similarly, from 0.225 g of aminophenylethylindone was obtained 0.380 g of a violet-red crystalline product (IX).

4. Preparation of product XI. 0.640 g of H-acid was dissolved in 150-200 ml of concentrated soda solution. A solution of the diazonium compound prepared from 0.446 g of aminodiphenylindone was then added under the conditions described in Experiment 2. Separation of the resulting product was carried out in a manner similar to that of the experiments already described. There was obtained 0.855 g (84.9% yield) of a dark violet crystalline powder with properties similar to those described for IV and VII.

Found %: N 6.34, 6.26. $C_{31}H_{19}O_3N_5S_2Na_2$. Calculated %: N 6.26.

5. Preparation of product XII. 0.223 g (0.00075 mole) of aminodiphenylindone was diazotized and coupled with 0.240 g (0.00075 mole) of H-acid by the method described in Experiment 3. After completion of the coupling reaction, the solution was alkalinized with sodium carbonate, and a diazotized solution of 0.223 g of aminodiphenylindone was added at a temperature of 2-5°. After stirring for several hours, the resulting dye was separated by the method described above. There was obtained 0.384 g (52.2% yield) of a black crystalline powder, slightly soluble in cold water and readily in hot, difficultly soluble in alcohol, and insoluble in benzene and ether. The product dissolved readily in nitrobenzene.

Found %: N 6.98, 6.92. $C_{32}H_{31}O_3N_5S_2Na_2$. Calculated %: N 7.15.

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ON THE PREPARATION OF ACETONE CYANOHYDRIN
(α -HYDROXYISOBUTYRONITRILE) FROM ACETONE
AND SODIUM CYANIDE*

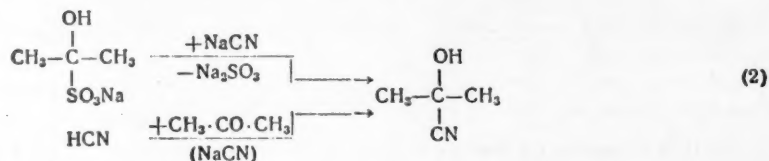
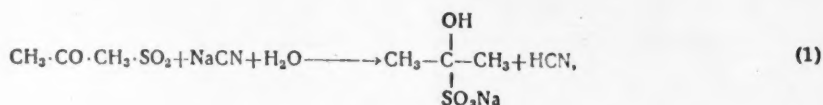
Vl. Kabaivanov and M. Mikhailov

(Presented by Academician I. N. Nazarov, June 27, 1957)

It is known that acetone cyanohydrin can be prepared from acetone and alkali metal cyanides by two routes: by the action of a mineral acid on a mixture of acetone and a solution of the alkali metal cyanide [1] or by the action of a preliminarily prepared bisulfite-addition compound of acetone on a solution of the alkali metal cyanide [2].

On the other hand, Raschig [3] established that acetone absorbs an equimolar amount of sulfur dioxide and forms the molecular compound $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \cdot \text{SO}_2$ with $d^4 = 1.08$, which on prolonged contact with water is converted to 2-hydroxy-2-propanesulfonic acid, and by interaction with solutions of alkali is readily converted to the bisulfite derivative.

Having in mind the facts mentioned above and also the circumstance that sulfurous acid is a stronger acid than hydrocyanic acid, as a result of which H_2SO_3 can displace HCN from its salts, we studied the possibility of preparing acetone cyanohydrin by means of the reaction of $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \cdot \text{SO}_2$ with acetone and NaCN in the presence of water according to the following equations:



It was established, by a large number of experiments, that these reactions proceed smoothly and practically to completion if they are carried out at a temperature below 25°.

* The authors express their appreciation to V. Yanchev for aid given during the experimental work.

In addition to this condition, it is also necessary to carry out the reaction in the presence of 8 moles of water per mole of $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \cdot \text{SO}_2$, and not in the presence of 1 mole of water as would appear from Equation (1), since the secondary product formed (1 mole of Na_2SO_3) adds 7 moles of water to form the crystal hydrate.

It was also established that by using the indicated amount of water, a large part of the NaCN, which is introduced into the process, goes into solution, and the cyanohydrin is obtained in the form of a product containing practically no water. On the introduction into the process of 20-30 % excess acetone, there is obtained an increase in yield to above 95% of the theoretical yield with respect to NaCN.

The excess acetone can be easily recovered by distillation of the resulting product.

Extraction of the acetone cyanohydrin, which is retained by the precipitated $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, is most expediently carried out by means of acetone.

The unreacted acetone as well as that used in the washing step can be used to replace part, or even all of the acetone required for new experiments.

The resulting acetone cyanohydrin, purified from unreacted acetone, has a concentration averaging about 95% and can be used in that condition as starting material for any synthesis. For example, methyl methacrylate was successfully synthesized from it.

The proposed method has the following basic advantages as compared to other methods described in the literature for the preparation of acetone cyanohydrin from acetone and NaCN:

1. While not less than 1 mole of mineral acid, or, correspondingly, NaHSO_3 , is required for the preparation of 1 mole of acetone cyanohydrin by the literature methods, SO_2 consumption in the new method comprises an average of $\frac{1}{2}$ mole.
2. The reaction product is obtained in the anhydrous state and does not require the additional drying necessary when the product is prepared in the aqueous medium of the other methods.
3. Owing to the absence, at the completion of the process, of an aqueous layer containing dissolved acetone cyanohydrin, the necessity of using an organic solvent for extraction of the product is obviated.
4. The yield of acetone cyanohydrin in the new method is considerably higher than in the other methods, which require that the work be carried out in aqueous medium.

EXPERIMENTAL METHODS

1. Saturation of acetone with sulfur dioxide. A specific amount of acetone was placed in an Erlenmeyer flask fitted with a rubber stopper containing two tubes, and saturated with cooled SO_2 from a cylinder. The gas-exit tube communicated by means of a rubber tube with the outside atmosphere for removal of the sulfur dioxide which had not been absorbed by the acetone at the completion of the process. Saturation was continued until weighings established that the acetone had absorbed an equimolar amount of SO_2 .

2. Preparation of acetone cyanohydrin. Into a 1-liter, three-necked flask fitted with a mercury seal, a mechanical stirrer, a dropping funnel, and a thermometer was placed 155 g of 95% NaCN, and 210 g of water and 150 g of 95% acetone were added. The latter can be partially or completely replaced by recovered acetone from previous experiments.

The flask containing the reaction mixture was cooled to below 25° by means of tap water. The stirrer was then started, and after 15 minutes the dropwise addition of 180 g of $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \cdot \text{SO}_2$ from the dropping funnel was begun. This amount of $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \cdot \text{SO}_2$ was added over a period of $1\frac{1}{2}$ hours while not permitting the temperature of the reaction mixture to rise above 25° .

The formation of a white precipitate of $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ began with the addition of the first portions of $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \cdot \text{SO}_2$. Later on, the soluble portion of the reaction product acquired the consistency of an oil and had a yellow color which gradually turned to orange.

After the addition of the $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \cdot \text{SO}_2$ was complete, the reaction mixture was stirred for an additional hour until it had an alkaline reaction (pH of 8-9 by universal indicator). The mixture was then filtered through a Buchner funnel.

Regardless of whether fresh acetone or recovered wash acetone from preceding experiments was used in the experiment, there was obtained 300-360 g of filtrate containing 70-73% acetone cyanohydrin, which comprised 80-84% of the theoretical yield with respect to NaCN.

By washing the precipitated $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ with pure acetone, another 100-130 g of filtrate containing 40-35% acetone cyanohydrin was obtained, which comprised 18-10% of the theoretical yield with respect to NaCN. It is obvious that the total yield was almost quantitative.

The major filtrate, to which could be added the wash acetone, was then acidified with concentrated sulfuric acid to a pH of 2 and distilled at 60-70° and 70 mm Hg to remove the unreacted acetone.

Under these conditions, we obtained acetone cyanohydrin with a concentration of 94-96% and also acetone containing 2-3% hydrogen cyanide. The average acetone cyanohydrin loss during distillation of the unreacted acetone was about 2-3%.

In the present work, the acetone cyanohydrin concentration was determined in all cases by the method of Liebig: 0.5 g of the product was dissolved in 25 ml of 10% KOH and titrated with 0.1 N AgNO_3 .

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**SYNTHESIS OF 4-HYDROXY-2,2,5,5-TETRAALKYL-3-FURANIDONES
BY REDUCTION OF
4-ISONITROSO-2,2,5,5-TETRAALKYL-3-FURANIDONES**

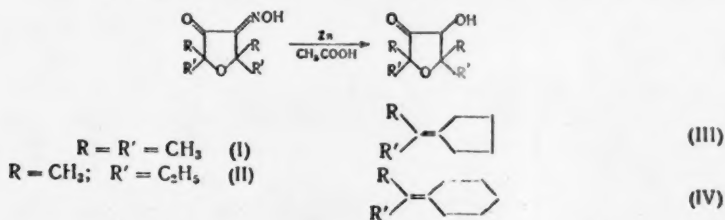
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(Presented by Academician A. N. Nesmeyanov, June 28, 1957)

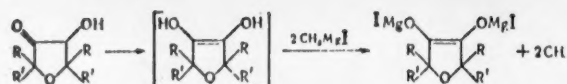
It is known from data in the literature that attempts to synthesize hydroxyketones of the furanidine [tetrahydrofuran] series - 4-hydroxy-3-furanidones [4-hydroxy-3-oxotetrahydrofuran] - have been unsuccessful [1, 2].

Since it did not appear possible to use for the synthesis of 4-hydroxy-2,2,5,5-tetraalkyl-3-furanidones [4-hydroxy-2,2,5,5-tetraalkyl-3-oxotetrahydrofurans] the methods usually used for the preparation of acyloins [3], we were obliged to search for other routes. It is well known that the action of reducing agents, for example, zinc dust and acetic acid [4, 5, 6], on isonitrosoketones of both the aliphatic and alicyclic series usually leads either to aminoketones or to products of their condensation. However, in 1941 Stodola noted an interesting case of an anomalous course of reaction when the product of the reduction of isonitrosodehydroisoandrosterone with zinc dust and 90% acetic acid proved to be hydroxydehydroisoandrosterone [7].

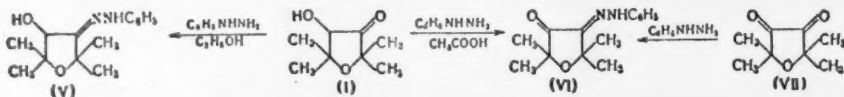
We established that on heating 4-isonitroso-2,2,5,5-tetraalkyl-3-furanidones for 6-7 hours with zinc dust and 50% acetic acid, not aminoketones, but hydroxyketones - 4-hydroxy-2,2,5,5-tetraalkyl-3-furanidones are formed in yields of 64-78%:



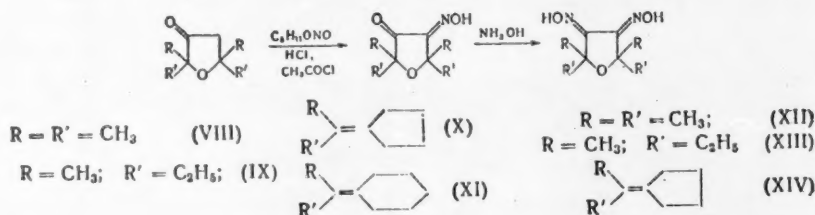
By determining the number of labile hydrogen atoms [8], we established the presence of two labile hydrogen atoms in 4-hydroxy-2,2,5,5-tetraalkyl-3-furanidones, which may be explained by the participation of the enediol form of 4-hydroxy-2,2,5,5-tetraalkyl-3-furanidones in the reaction with excess methylmagnesium iodide:



This is confirmed by the fact that we detected only one labile hydrogen atom in 2,2,5,5-tetramethyl-3-furanidone. The phenylhydrazone of 4-hydroxy-2,2,5,5-tetramethyl-3-furanidone (V) is formed by the reaction of 4-hydroxy-2,2,5,5-tetramethyl-3-furanidone (I) with phenylhydrazine in alcoholic solution, while in acetic acid medium the monophenylhydrazone of 2,2,5,5-tetramethyl-3,4-furanidinedione (VI) which is identical with that formed from 2,2,5,5-tetramethyl-3,4-furanidinedione [2,2,5,5-tetramethyl-3,4-dioxotetrahydrofuran] (VII), is formed. This reaction - oxidation by phenylhydrazine of a hydroxyl group next to a carbonyl group - also confirms the structure of the hydroxyketones obtained by us.



It should be noted that the impossibility of preparing diphenylhydrazones (osazones) of α -diketones of the furanidine series was noted earlier by T. I. Temnikova and P. A. Tikhomolov [9]. We obtained the original 4-isonitroso-2,2,5,5-tetraalkyl-3-furanidones (VIII - XI) in yields of 49-89% by the action of isoamyl nitrite on a mixture of 2,2,5,5-tetraalkyl-3-furanidones, acetyl chloride, and hydrochloric acid in the cold.



By the action of hydroxylamine on these compounds, we obtained the dioximes of the corresponding 3,4-furanidinediones (XII - XIV) [3,4-dioxotetrahydrofurans], which were identical with those described in the literature [10, 11]. The structure of 4-isonitroso-2,2,5,5-tetramethyl-3-furanidone (VIII) was confirmed by alternate synthesis from 2,2,5,5-tetramethyl-3,4-furanidinedione (VII) and the equivalent amount of hydroxylamine.

It must be noted that 4-isonitroso-2,2,5,5-tetraalkyl-3-furanidones have higher melting points immediately after separation than after recrystallization or lengthy standing. Changes in the m. p. of 4-isonitroso-2,2,5,5-tetramethyl-3-furanidone are shown below:

Standing time, hours	0	8	24	74	146	212	260	300
Melting point, °C	129	122	118	107	100	97	97	97

Cases of changes in the melting points of isonitroso compounds have been reported in the literature [12, 13]. Without resolving the question of the spatial configuration of the 4-isonitroso-3-furanidones prepared by us, we assume that the changes in their melting points were due to a transition from one form to another, more favored energetically. Undoubtedly, this explains why the melting point of the 4-isonitroso-2,2,5,5-tetramethyl-3-furanidone (VIII) prepared by us differs from the melting point of the only representative of this class of compounds described in the literature - 4-isonitroso-2,2,5,5-tetramethyl-3-furanidone [1].

TABLE 1

Substance	Melting point, °C		Found %			Calculated %		
	experimental	literature	C	H	N	C	H	N
4-Isonitroso-2,2,5,5-tetra-methyl-3-furanidone (VIII) (yield 79%)	105-106 (from CCl_4) 96-97 (from C_6H_6)	167-170 [1]	56.37 56.41 56.15 55.92	7.89 7.66 7.79 7.66	8.34 8.23 7.99 8.04	56.12 56.12	7.65 7.65	8.18 8.18
2,4-Dinitrophenylhydrazones of VIII (from aqueous alcohol)	236-237	-			19.88 19.77			19.64
Dioxime of 2,2,5,5-tetra-methyl-3,4-furanidone-dione (XII) (from alcohol)	223-224	223-224 [10]						
4-Isonitroso-2,5-dimethyl-2,5-diethyl-3-furanidone (IX)* (yield 49%) (from petroleum ether)	72-73	-	55.10 55.19	8.81 8.70	6.48 6.49	55.28	8.81	6.40
Dioxime of 2,5-dimethyl-2,5-diethyl-3,4-furanidone-dione (XII) (from aqueous alcohol)	192-193	193 [10]						
4-Isonitroso-2,2,5,5-bis-tetra-methylene-3-furanidone (X)** (yield 89%) (from petroleum ether)	97-100	-			6.04 6.19			6.28
Dioxime of 2,2,5,5-bis-tetra-methylene-3,4-furanidone-dione (XIV) (from aqueous alcohol)	198	198-199 [11]	66.59 66.62	8.55 8.49	5.78 5.93	66.90	8.42	5.57
4-Isonitroso-2,2,5,5-bis-penta-methylene-3-furanidone (XI) (yield 66%) (from cyclohexane)	137-140	-						

* Compound isolated in the form of the monohydrate - $\text{C}_{10}\text{H}_{17}\text{O}_3\text{N} \cdot \text{H}_2\text{O}$.

** Nitrosation carried out in isomyl alcohol.

TABLE 2

Substance	Boiling point, °C/mm Hg	Melting point, °C	Found %			Calculated %			Number of labile H atoms
			C	H	N	C	H	N	
4-Hydroxy-2,2,5,5-tetramethyl-3-furanidone (I) (yield 78%) (from petroleum ether)	—	98.5-99	60.80 60.74	8.99 9.03	— —	60.74	8.92	—	2.162 2.204
2,4-Dinitrophenylhydrazones of I (from aqueous alcohol)	—	187-188	49.49 49.63	5.57 5.44	16.34 16.38	49.70	5.38	16.56	—
Phenylhydrazone of I (from n-octane)	—	136-137	—	—	11.47 11.50	—	—	11.28	—
Monophenylhydrazone of 2,2,5,5-tetramethyl-3,4-furandione (VI) (from alcohol)	—	96-97	68.35 68.11	7.56 7.47	11.39 11.45	68.28	7.37	11.35	—
4-Hydroxy-2,5-dimethyl-2,5-diethyl-3-furanidone (II) * (yield 64%)	75- 76/3 mm	—	64.60 64.70	10.11 10.02	—	64.48	9.74	—	2.176 2.091
2,4-Dinitrophenylhydrazone of II (from alcohol)	—	145-146.5	52.83	5.95	15.70 15.66	52.60	5.79	15.34	—
4-Hydroxy-2,2,5,5-bis(methylene-3-furanidone (III) (yield 73%)	112- 113/3 mm	47-48	68.54 68.46	8.63 8.67	—	68.54	8.63	—	1.989 2.090
2,4-Dinitrophenylhydrazone of III (from aqueous alcohol)	—	177	—	—	14.33 14.31	—	—	14.35	—
4-Hydroxy-2,2,5,5-bis(methylene-3-furanidone (IV) (yield 73%) (from n-hexane)	—	75-76	70.81 70.78	9.48 9.52	—	70.55	9.30	—	—
2,4-Dinitrophenylhydrazone of IV (from alcohol)	—	211	57.72 57.71	6.44 6.30	12.98 13.18	57.40	6.26	13.39	—

* n_D^{20} 1.4531; d_4^{20} 1.0221; MR_D 49.28. $C_{10}H_{15}O_3$. Calculated MR_D 49.51.

The 4-hydroxy-2,2,5,5-tetraalkyl-3-furanidones and 4-isonitroso-2,2,5,5-tetraalkyl-3-furanidones prepared by us have not been described in the literature.

EXPERIMENTAL METHODS

4-Isonitroso-2,2,5,5-tetraalkyl-3-furanidones (VIII-XI). 0.22 mole of isoamyl nitrite was added, with stirring, at a rate of 0.5 ml/minute * to a mixture of 0.14 mole of 2,2,5,5-tetraalkyl-3-furanidone [10, 11], 5 ml of concentrated hydrochloric acid, and 4 ml of acetyl chloride. The last 2-3 ml of isoamyl nitrite was added more slowly and while cooling the reaction mixture with ice water; stirring was continued for another 30 minutes, and then for 1 hour while cooling with ice and salt.** The precipitate was filtered and recrystallized. The constants and yields of the 4-isonitroso-2,2,5,5-tetraalkyl-3-furanidones and their derivatives are presented in Table 1.

Alternate synthesis of 4-isonitroso-2,2,5,5-tetramethyl-3-furanidone. 3.1 g (0.02 mole) of 2,2,5,5-tetramethyl-3,4-furanidinedione (VII) and 1.4 g (0.02 mole) of hydroxylamine hydrochloride were refluxed for 2 hours in a mixture of 10 ml of pyridine and 5 ml of absolute alcohol. The precipitate, which separated on pouring the mixture into 150 ml of cold water, was refluxed with benzene; the material insoluble in benzene, m. p. 223-224° (from alcohol), was the dioxime of 2,2,5,5-tetramethyl-3,4-furanidinedione. Cooling of the benzene solution precipitated crystals of 4-isonitroso-2,2,5,5-tetramethyl-3-furanidone with a m. p. of 96-97° (from benzene). A mixed sample with the 4-isonitroso-2,2,5,5-tetramethyl-3-furanidone prepared by nitrosation of 2,2,5,5-tetramethyl-3-furanidone showed no melting point depression.

4-Hydroxy-2,2,5,5-tetraalkyl-3-furanidones (I-IV). Into a flask fitted with a reflux condenser and a stirrer were placed 0.05 mole of 4-isonitroso-2,2,5,5-tetraalkyl-3-furanidone and 100 ml of 50% acetic acid. After the addition of the first portion of zinc dust, the reaction mixture was heated until the reaction was initiated, and the remaining part of the zinc dust (0.28 g-atoms total) was added gradually. Refluxing and stirring were continued for another 6-7 hours, after which the reaction mixture was diluted with 120 ml of water, neutralized to a pH of 6, and extracted with ether. After distillation of the ether, the ether extracted material was dried with anhydrous sodium sulfate, and the 4-hydroxy-2,2,5,5-tetraalkyl-3-furanidone was separated. The constants and yields of the 4-hydroxy-2,2,5,5-tetraalkyl-3-furanidones are presented in Table 2.

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* The nitrosation of 2,2,5,5-tetramethyl-3-furanidone can be carried out at a rate of 2.5 ml/minute.

** Good yields of isonitrosoketones are obtained by careful observance of the rate of introduction of isoamyl nitrite and of the temperature regime.

*** Original Russian pagination. See C. B. Translation.

**** In Russian.

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SYNTHESIS OF ACETYL-2-CHLOROCYCLOALKENES

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(Presented by Academician A. N. Nesmeyanov, June 27, 1957)

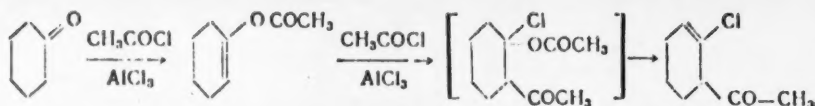
A method was recently developed in our laboratory for the synthesis of β -chlorovinyl ketones of the aliphatic and aromatic series [1, 2], and their transformations, widely used in syntheses, were studied [3]. In order to augment our knowledge of this important class of compounds, it appeared of interest to prepare aliphatic β -chlorovinyl ketones and compounds similar to them. There is an indication in the patent literature [4] that acetyl-2-chlorovinyl-1-cyclohexene is formed during the interaction of cyclohexanone and acetyl chloride. On the other hand, in a brief note appearing recently, Jacquier [5] indicated, without any experimental details, that the sole product of this reaction is acetyl-2-chloro-2-cyclohexene; the author further asserted that on subsequent refluxing with dimethylaniline it is converted to acetyl-2-chloro-1-cyclohexene.

We studied this reaction in detail, and we found that the product is, in reality, a mixture of substances (yield 82%) consisting chiefly of acetyl-2-chloro-2-cyclohexene. This conclusion was reached on the basis that the reaction product on treatment with semicarbazide gives a mixture of two semicarbazones, from which is readily isolated as the major product a semicarbazone with a m. p. of 158°, readily soluble in benzene, and coinciding completely in properties with the semicarbazone of acetyl-2-chloro-2-cyclohexene described by Mousseron [6]. The second semicarbazone was formed in small amounts and was insoluble in benzene; it could not be isolated in the pure form and melted over a broad range with decomposition, which permitted the assumption that it is the semicarbazone of acetyl-2-chloro-1-cyclohexene, since it is well known that semicarbazones of β -chlorovinyl ketones change their melting point owing to cyclization to pyrazole derivatives [1].

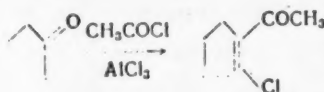
In accordance with the statement of Jacquier [5], we attempted to carry out the rearrangement of acetyl-2-chloro-2-cyclohexene to the corresponding α , β -unsaturated isomer by refluxing with dimethylamine; however, we became convinced that such isomerization does not take place.

We were able to arrive at certain conclusions regarding the mechanism of the reaction of cyclohexanone with acetyl chloride. Turning our attention to the fact that good yields are obtained only at a molar ratio of cyclohexanone to acetyl chloride of 1:2 or higher, we assumed that, under the conditions of the reaction, the enol acetate of cyclohexanone is formed first (the formation of which under these conditions is quite probable [7, 8]), which then adds a molecule of acetyl chloride by the Kondakov-Krapivin type reaction which is general to unsaturated compounds.

This assumption was confirmed by the formation, in high yields, of acetyl-2-chloro-2-cyclohexene by the reaction of equimolar amounts of the enol acetate and acetyl chloride under similar conditions. The assumption that acetyl-2-chloro-2-cyclohexene is formed simply by rearrangement of the enol acetate with subsequent enolization and replacement of the hydroxyl group by chlorine under the influence of aluminum chloride must be refuted, since treatment of the enol acetate of cyclohexanone with aluminum chloride under our conditions did not result in the formation of acetyl-2-chloro-2-cyclohexene. Thus, it must be possible to represent the reaction of cyclohexanone with acetyl chloride by the following:



We were able to extend this reaction to the cyclopentane series. The product of the reaction of cyclopentanone with acetyl chloride under analogous conditions is acetyl-2-chloro-1-pentene – the first representative of the cyclic β -chlorovinyl ketones. This is indicated by the high reactivity of the substance obtained, the exaltation of the molecular refraction, and of the formation of a salt with triethylamine and of a pyrilium salt – all of which are marks characteristic of β -chlorovinyl ketones [1, 9].*



Thus, the reaction of acetyl chloride with cyclohexanone gives a β , γ -unsaturated chloroketone, while with cyclopentanone it gives an α , β -unsaturated isomer; this difference probably has a direct connection with the peculiarities of conformation of the cyclohexanone and cyclopentanone rings.

For a final conclusion, we compared the ultraviolet absorption spectra of the 2,4-dinitrophenylhydrazones of the preparations of acetyl-2-chloro-2-cyclohexene and acetyl-2-chloro-1-cyclopentene.** As is well known [10], the u. v. spectra (in the region of 300–400 $m\mu$) of 2,4-dinitrophenylhydrazones of α , β -unsaturated ketones in isoctane solution are characterized by a shift of the maximum of approximately 17 $m\mu$ in comparison with the maximum in the spectrum of the derivative of a β , γ -unsaturated ketone. The 2,4-dinitrophenylhydrazone of acetyl-2-chloro-2-cyclohexene had λ_{\max} 344 $m\mu$, and the 2,4-dinitrophenylhydrazone of acetyl-2-chloro-1-pentene had a maximum at 362 $m\mu$. Similar shifts in the spectra were also observed for alcoholic solutions (365 and 394 $m\mu$, respectively).

This reaction as applied to other ketones is currently under investigation by us.

EXPERIMENTAL METHODS

1. Reaction of cyclohexanone with acetyl chloride. In a three-necked flask fitted with a reflux condenser and a dropping funnel were placed 151 g (1.16 mole) of $AlCl_3$ and 75 cc of dry dichloroethane. While stirring vigorously and cooling with water, a mixture of 36.5 g (0.39 mole) of cyclohexanone and 86 g (1.16 mole) of acetyl chloride was added, the mixture was stirred for an additional 18 hours, and was then poured into a mixture of ice and concentrated hydrochloric acid. An oily layer separated; the water layer was extracted with dichloroethane. The combined extracts were washed with water and dried over $CaCl_2$. The solvent was distilled; the residue was distilled under vacuum, and a fraction boiling at 105–120°/20 mm was collected. After a second distillation, 49.5 g (82% calculated on cyclohexanone) of a substance with a b. p. of 124–129°

* Mousseron [6] prepared a substance to which he assigned the structure of acetyl-2-chloro-1-cyclopentene; however, he did not present in the article any analytical data for this substance, analyses of the semicarbazone for nitrogen had a discrepancy of 5%, and the molecular refraction varied by several units; as a result of this, one can only think that the author did not have at hand the pure compound of the indicated structure.

** The u. v. spectra were obtained in the laboratory headed by L. A. Kazitsina, for which the authors expressed their deep appreciation.

per 30 mm was obtained. After a third distillation, we obtained a fraction with a b. p. of 108-109°/15 mm; n_D^{20} 1.4985; d_4^{20} 1.1232; MR_D 41.38, $C_8H_{11}OClF \cdot MR_D$ calc. 41.35.

Found %: C 60.33, 60.33; H 7.09, 7.09; Cl 22.29, 22.46, $C_8H_{11}ClO$. Calculated %: C 60.56; H 7.00; Cl 22.35.

The semicarbazone prepared from the fraction boiling at 124-129°/30 mm had a m. p. of 136-138°. Of 22 g of the semicarbazone, a large part (20 g) dissolved in benzene, and after recrystallization from it had a m. p. of 158°.

Found %: N 19.73, 19.87, $C_8H_{11}ON_3Cl$. Calculated %: N 19.48.

Literature data [6]: m. p. 158-159°.

The benzene-insoluble remainder (2 g) melted over a broad range with decomposition.

The 2,4-dinitrophenylhydrazine was obtained according to [10]; m. p. 128-129° (from alcohol). Literature data [5]: m. p. 128-129°.

2. Similarly, from 196 g (2 moles) of cyclohexanone, 314 g (4 moles) of acetyl chloride, and 534 g (4 moles) of aluminum chloride in 475 cc of dichloroethane was obtained 201 g (64%) of 2-chloro-1-acetyl-2-cyclohexene (with some admixture of 2-chloro-1-acetyl-1-cyclohexene); b. p. 110-120°/20 mm, n_D^{20} 1.4961.

3. Similarly, from 49 g (0.5 mole) of cyclohexanone, 39 g (0.5 mole) of acetyl chloride, and 67 g (0.5 mole) of aluminum chloride was obtained on distillation: 22.2 g of cyclohexanone, b. p. 58-59°/24 mm, n_D^{20} 1.4515; 8.4 g of a fraction with a b. p. of 150-151°/21 mm, n_D^{20} 1.5079, d_4^{20} 1.0072; its constants are close to the constants of cyclohexylidenecyclohexanone [11]: b. p. 148-150°/20 mm, n_D^{20} 1.5062, d_4^{20} 1.004.

4. Attempted isomerization of acetylchloro-2-cyclohexene to acetyl-2-chloro-1-cyclohexene. 30 g of the substance from Experiment No. 1 which consisted chiefly of acetylchloro-2-cyclohexene, and 50 g of dimethylaniline were refluxed for 24 hours. The reaction mixture was washed with dilute hydrochloric acid and water. It was dried over $CaCl_2$. Upon distillation there was obtained 16.5 g of a product with a b. p. of 93-100°/10 mm, n_D^{20} 1.4990; semicarbazone, m. p. 157.5-158°.

5. Reaction of the enol acetate of cyclohexanone with acetyl chloride. 30 g (0.215 mole) of the enol acetate of cyclohexanone in a mixture with 30.5 cc (33.5 g, 0.43 mole) of acetyl chloride was added to a suspension of 57 g (0.43 mole) of aluminum chloride in 100 cc of dichloroethane. After stirring for 5 hours, the mixture was treated as in Experiment No. 1. 14.6 g of acetyl-2-chloro-2-hexene was obtained. B. p. 115-125°/25 mm, n_D^{20} 1.5000; semicarbazone, m. p. 158.5-159°; did not show a melting point depression when mixed with the semicarbazone from Experiment No. 1.

6. Reaction of cyclopentanone with acetyl chloride.

a. In dichloroethane solution. To 134 g (0.5 mole) of $AlCl_3$ in 250 cc of dichloroethane were added, while cooling with ice, 78.5 g (1 mole) of acetyl chloride and then 42 g (0.5 mole) of cyclopentanone. After stirring for 2 hours, the mixture was treated in the usual manner.

On distillation there were obtained 21.7 g of cyclopentanone, b. p. 38-40°/25 mm; 10.6 g (15% calculated on the cyclopentanone taken, 31% calculated on the cyclopentanone reacted) of acetyl-2-chloro-1-cyclopentene. B. p. 91-92°/22 mm, n_D^{20} 1.5045, d_4^{20} 1.1429, MR_D 37.45, C_7H_9ClO calculated 35.74.

Found %: C 58.18, 58.35; H 6.50, 6.35, C_7H_9ClO . Calculated %: C 58.20; H 6.28.

The semicarbazone decomposed without melting. 2,4-Dinitrophenylhydrazine, m. p. 174-175° (from glacial CH_3COOH).

b. In carbon disulfide solution. Similarly, from 21 g of cyclopentanone, 35.5 cc of acetyl chloride and 67 g of $AlCl_3$ in 100 cc of carbon disulfide was obtained 7.9 g (22% of theoretical) of acetyl-2-chloro-1-pentene, b. p. 100-101°/30 mm, n_D^{20} 1.5061.

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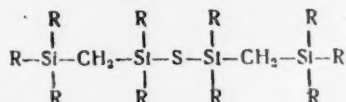
* Original Russian pagination. See C. B. Translation.

PREPARATION OF COMPOUNDS WITH SILTHIANE-CARBON LINKS

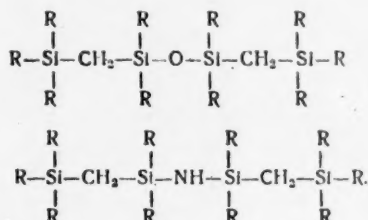
N. S. Nametkin, Academician A. V. Topchiev, and L. S. Povarov

There have appeared, in recent years, a number of papers on the synthesis of organosilicon compounds containing sulfur connected to a silicon atom. It has been proposed to prepare similar compounds by the reaction of halogen derivatives of silicon with metal sulfides [1, 2] and also by the action of hydrogen sulfide on primary aminosilanes [3, 4] or trialkylchlorosilanes [5].

It appeared to us to be of interest to synthesize compounds with silthiane-carbon links



and to study their properties in comparison with compounds of similar structure previously described by us but containing siloxane-carbon [6-8] and silazine-carbon links [9]:



Starting materials for the preparation of compounds with silthiane-carbon links were the pentaalkylbromo derivatives of disilanemethane previously described by us [6] and prepared by the reaction of pentaalkyl derivatives of disilanemethane with bromine.

We showed that the treatment of pentamethylbromodisilanemethane [2-bromo-2,4,4-trimethyl-2,4-disilapentane] with hydrogen sulfide in the presence of pyridine yields a mixture of pentamethylthioldisilanemethane [2,4,4-trimethyl-2,4-disilapentane-2-thiol] and bis-(pentamethyldisilanemethane)-sulfide [2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasilane-5-thianonane] according to

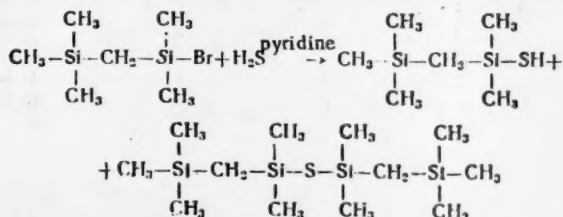
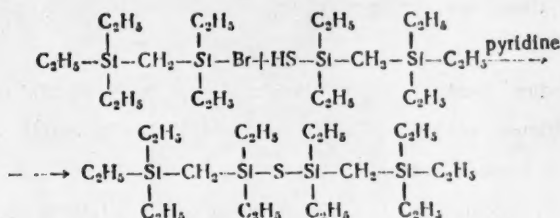


TABLE 1

Pentaalkylthiol Derivatives of Disilane-methane and Bis(Pentaalkyldisilane-methane-Sulfides)

	Formula	Boiling point		Solidifica- tion point, °C	d^{20}_4	n^{20}_D	$M_R D$	
		°C	mm Hg				found	calc.
Pentamethylthiol-disilane- methane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{Si}-\text{CH}_2-\text{Si}-\text{SH} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	58-60	14	—	0.8632	1.4604	56.53	56.75
Pentaethylthiol-disilane- methane	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{C}_2\text{H}_5-\text{Si}-\text{CH}_2-\text{Si}-\text{SH} \\ \quad \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	113-114	3.5	—	0.8989	1.4852	79.02	80.3
Bis(pentamethylthiol-disilane- methane)sulfide	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{CH}_3-\text{Si}-\text{CH}_2-\text{Si}-\text{S}-\text{Si}-\text{CH}_2-\text{Si}-\text{CH}_3 \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	117-118	3.5	-98	0.8774	1.4777	103.84	104.96
Bis(pentaethylthiol-disilane- methane)sulfide	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \quad \quad \\ \text{C}_2\text{H}_5-\text{Si}-\text{CH}_2-\text{Si}-\text{S}-\text{Si}-\text{CH}_2-\text{Si}-\text{CH}_3 \\ \quad \quad \quad \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	202-204	3	-85	0.9108	1.4980	149.00	150.06

Pentaethylbromodisilanemethane yields only pentaethylthiodisilanemethane on treatment with hydrogen sulfide. We obtained bis(pentaethylthiodisilanemethane) sulfide by the reaction of pentaethylbromodisilanemethane with pentaethylthiodisilanemethane in the presence of pyridine:



The properties of the sulfur-containing organosilicon compounds prepared by us are presented in Table 1.

EXPERIMENTAL METHODS

I. A solution of 13.6 g (0.17 mole) of pyridine in 100 ml of ether was saturated with hydrogen sulfide over a period of 30 minutes, the hydrogen sulfide having been dried with calcium chloride. A solution of 40 g (0.17 mole) of pentamethylbromodisilanemethane in 50 ml of ether was then added. The mixture was heated to boiling for 5 hours while passing a weak stream of hydrogen sulfide through it. The mixture was cooled, the precipitate of pyridine hydrobromide filtered, and, after distillation of the ether, the liquid reaction products were distilled into the following fractions:

1) Fraction boiling at 58-60° at 14 mm; pentamethylthiodisilanemethane; 11 g obtained (yield 36.4%).

Found %: C 41.02, 41.02; H 9.71, 9.81; S 17.34, 17.80. $\text{C}_6\text{H}_{13}\text{SSi}_2$. Calculated %: C 40.39; H 10.17; S 17.98.

2) Fraction boiling at 117-118° at 3.5 mm; bis(pentamethylthiodisilanemethane) sulfide; 11.5 g obtained (yield 41.9%).

Found %: C 44.82, 44.84; H 10.60, 10.59; S 10.39, 9.84. $\text{C}_{12}\text{H}_{24}\text{SSi}_4$. Calculated %: C 44.76; H 10.64; S 9.93.

Molecular weight (cryoscopic method; benzene solvent): M found, 315, 324; M calc., 322.7.

II. 1) Hydrogen sulfide was passed for 30 minutes through a solution of 20 g (0.25 mole) of pyridine in 150 ml of toluene, after which 72 g (0.25 mole) of pentaethylbromodisilanemethane was added. The reaction mixture was heated to boiling for 12 hours while passing a weak stream of hydrogen sulfide through it. The mixture was cooled, the precipitate of pyridine hydrobromide filtered, and the filtrate was distilled. After distillation of the toluene, there was obtained 48 g (yield 80.3%) of pentaethylthiodisilanemethane; b. p. 113-114° at 3.5 mm.

Found %: C 53.52, 53.72; H 10.69, 10.77; S 12.52, 12.39. $\text{C}_{11}\text{H}_{23}\text{SSi}_2$. Calculated %: C 54.26; H 9.52; S 13.27.

2) To a mixture of 17.5 g (0.07 mole) of pentaethylthiodisilanemethane and 5.6 g (0.07 mole) of pyridine in 50 ml of toluene was added 30 g (0.07 mole) of pentaethylbromodisilanemethane in 25 ml of toluene. The reaction mixture was heated to boiling for 16 hours. The mixture was cooled, the pyridine hydrobromide was filtered, and the toluene distilled. Distillation of the liquid reaction products gave 10.5 g (yield 32.4%) of a substance with a b. p. of 202-204° at 3 mm which was bis(pentaethylthiodisilanemethane) sulfide.

Found %: C 57.61, 57.39; H 11.87, 11.70; S 6.44, 6.55. $\text{C}_{22}\text{H}_{44}\text{SSi}_4$. Calculated %: C 57.08; H 11.76; S 6.92.

Molecular weight (cryoscopic method; benzene solvent): M found 457, 469; M calc. 463.

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REACTION OF DIALKOXYTITANIUM OXIDES WITH TETRAALKOXYASILANES

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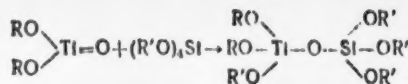
In 1954, we described for the first time representatives of the dialkoxytitanium oxides [1], $(RO)_2TiO$, which were prepared by oxidation of trialkoxytitaniums with atmospheric oxygen. The question of whether these compounds are monomeric and have the structure $(RO)_2Ti=O$, or whether they are polymeric, $[(RO)_2TiO]_{2n}$, is still open.

TABLE 1
Results of Molecular Weight Determinations on the Dialkoxytitanium Oxides

Substance investigated	Solvent	Concentration of solution, %	Molecular weight	
			calc.	found
Isopiestic method (azobenzene standard)				
$(n-C_3H_7O)_2TiO$	Benzene	0.1001	182	210
$(n-C_4H_9O)_2TiO$	"	0.1070	209.9	243
Cryoscopic method				
$(n-C_3H_7O)_2TiO$	Dioxane	0.7	182	259
$(n-C_4H_9O)_2TiO$	Benzene	0.67	209.9	206.4
				218.7

Association in solution of organic derivatives of orthotitanic acid (containing radicals of normal structure) is a characteristic property of this class of compounds [2-5]; therefore, determination of the molecular weights of these substances by cryoscopic or ebullioscopic methods almost always gives values which are sharply increased over those calculated for the monomeric form. The isopiestic method of determining molecular weights [6] permits working with solutions of 0.1% concentration; in such solutions, association of titanium-containing organic compounds occurs to a very much lesser extent. Using the isopiestic method, we established that the dialkoxytitanium oxides are monomeric (see Table 1), at least in such dilute solutions. The monomeric state of the latter leads, of necessity, to the presence in these compounds of a double bond between the titanium and oxygen atoms. This fact is very interesting, since, up to the present, only a small number of structures in which a transition element must have a π -bond are known. Nor have there yet been distinguished among organosilicon compounds any substances containing a silicon doubly bonded with an oxygen. While studying the products of the decomposition of dialkylpolysiloxanes, $(R_2SiO)_n$, K. A. Andrianov and N. N. Sokolov [7] observed the formation of dialkylsilanones, R_2SiO , but only in a mass spectrometer.

The presence of the double bond in dialkoxytitanium oxides permits one to expect addition at this bond. Indeed, it appeared possible to carry out the addition of tetraalkoxysilanes with the formation of molecules containing titanium and silicon according to the reaction



A substance with the chain O—Ti—O—Si—O, but having a more complex structure, namely tetrakis(trimethylsiloxy)titane, has been described in the literature [8, 10]. It was prepared by the action of trimethylsilanol on titanium tetrachloride in the presence of ammonia. Also, polymers have been described [9, 10] in which the molecular chain consists of silicon, titanium, and oxygen atoms.

There are also a number of patents in which polymers of such type are described [11].

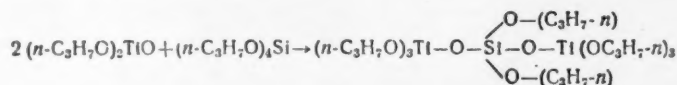
The addition of tetraalkoxysilanes to dialkoxytitanium oxides proceeds readily on heating a mixture of the substances for a short time. We carried out the addition of tetra-*n*-propoxysilane to di-*n*-propoxytitanium oxide.

To a solution of 5.5 g (0.030 mole) of di-*n*-propoxytitanium oxide in *n*-hexane was added 80 g (0.030 mole) of tetra-*n*-propoxysilane. As always when working with organic compounds containing titanium, all operations were carried out with complete exclusion of moisture. The reaction mixture was refluxed 4 hours; after distillation of the solvent and unreacted tetra-*n*-propoxysilane, the product was distilled. B. p. 66–69° at 10⁻⁵ mm and 125–126° at 1 mm; n_D^{20} 1.4647; the yield was 29% of theoretical.

Found %: C 48.66, 48.66, 48.62; H 9.63, 9.82, 9.47; ash 30.62, 30.67. $\text{C}_{18}\text{H}_{32}\text{O}_7\text{TiSi}$.
Calculated %: C 48.42; H 9.48; ash 31.35.

Found M 667 (isopiestic method in *n*-C₃H₇OH); calculated M 446.6.

The following reaction was carried out next:

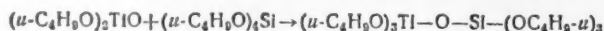


The experiment was carried out in a manner similar to the preceding. 6.9 g (0.038 mole) of di-*n*-propoxytitanium oxide and 5 g (0.019 mole) of tetra-*n*-propoxysilane were used in the reaction. The product obtained boiled at 78–81° at 10⁻⁵ mm, n_D^{20} 1.4910; the yield was 36% of theoretical.

Found %: C 45.92, 45.73; H 9.13, 9.07; ash 34.90, 35.01. $\text{C}_{24}\text{H}_{56}\text{O}_{10}\text{Ti}_2\text{Si}$. Calculated %: C 45.85; H 8.98; ash 34.98.

Found M 1060 (isopiestic method in *n*-C₃H₇OH), calculated M 740.

The addition of tetraisobutoxysilane to diisobutoxytitanium oxide was carried out next:



The diisobutoxytitanium oxide was prepared by hydrolysis of isobutylorthotitanate [5]. The experiment was carried out in a manner similar to the preceding. 8.2 g (0.039 mole) of diisobutoxytitanium oxide and 12.56 g (0.039 mole) of tetraisobutoxysilane were introduced into the reaction.

In this case, after distillation of the solvent and unreacted tetraisobutoxysilane, a precipitate formed in the reaction mixture. It was filtered. The filtrate was distilled under vacuum. This gave a product boiling at 75–78° at 10⁻⁵ mm; n_D^{20} 1.4610.

Found %: C 54.47, 54.53, 54.58; H 10.46, 10.71, 10.42; ash 25.89, 25.75. $\text{C}_{24}\text{H}_{56}\text{O}_7\text{TiSi}$.
Calculated %: C 54.2; H 10.2; ash 26.4.

It should be mentioned that this material decomposed during an attempt to distill it at a residual pressure of 1 mm. This gave isobutyl orthotitanate. B. p. 123–124° at 1 mm (literature data [5]; b. p. 123° at 0.7 mm).

Found %: C 56.12, 56.01; H 11.17, 11.04.

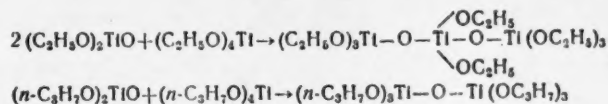
From another sample

Found %: C 56.9, 57.02; H 10.73, 10.85. $C_{16}H_{36}O_4Ti$. Calculated %: C 56.45; H 10.66.

We still have not determined the structure of the second product of this reaction (which precipitated from the reaction mixture). The substance was easily recrystallized from n-hexane and melted at 193-195°.

Found %: C 40.75, 41.04; H 7.99, 8.03.

We also carried out the addition of alkyl orthotitanates to dialkoxytitanium oxides:



In both cases, after recrystallization, analyses of the products obtained corresponded, respectively, to octaethoxytrinititanoxane and hexa-n-propoxydititanoxane. Investigation of them continues.

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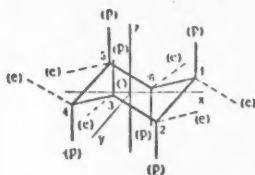
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OPTICAL INVESTIGATION OF TRANSFORMATIONS OF CIS- AND TRANS-2-METHYL-1-ETHYLCYCLOHEXANOLS

M. I. Batuev, A. A. Akhrem, A. D. Matveeva
and Academician I. N. Nazarov*

1. Investigations of the last 10-15 years have shown that cyclohexane exists predominantly in the chair form [1-6] in which it possesses minimum energy. The potential barrier of the conversion of the chair form into the boat form has been evaluated at from 5.6 [5] to 9-10 kcal/mole [4].



Kohlrausch (1936) and Hassel (1943) first observed [1] that the C-H bonds of the chair form of cyclohexane can be divided into two groups: 1) parallel to the OZ axis and 2) making an angle of $\pm 19.5^\circ$ ($109.5^\circ - 90^\circ$) with the OXY plane. The bonds of the first group are now called axial and are denoted by the letter *a*, and those of the second group are called equatorial and are denoted by the letter *e*. Carbon atoms 1, 3, 5, and 2, 6, 4, lie in two parallel OXY planes with a distance of 0.5 Å between them. In the chair form of cyclohexane, each equatorial hydrogen atom is found at a distance of ~ 2.5 Å

from the neighboring two axial and two equatorial hydrogen atoms (1,2-interaction). Each axial hydrogen atom is found at approximately this same distance from the two hydrogen atoms of the two neighboring equatorial C-H bonds (1,2-interaction) and from the two neighboring axial bonds located on the same side of the ring (1,3-interaction). This distance is approximately equal to twice the van der Waals radius of a hydrogen atom; therefore the force of repulsion between these hydrogen atoms is small. This promotes energetic preference of the chair form over the boat form, for which this distance (~ 1.83 Å) is less than the sum of two van der Waals radii for hydrogen atoms.

All six of the axial hydrogen atoms of the ring can convert to equatorial and vice versa without rupture of the carbon-carbon bonds during the conversion.** The potential barrier for this conversion is small in cyclohexane. However, the situation is substantially different in the case of mono-substituted cyclohexanes. Substituents with larger van der Waals radii than that of the hydrogen atom are subject to substantial repulsive forces as a result of 1,2- and 1,3-interactions, and equatorial substitution becomes favored energy-wise: 1e for mono-substituted, 2e for ortho-disubstituted, etc. This preference was confirmed experimentally (electron diffraction) by Hassel [1], which permitted him to formulate the following rule: the most stable

* Deceased.

** The different spatial forms of molecules which can be converted one into the other merely by means of the appropriate rotation of atoms without rupture of interatomic bonds are called conformations.

isomer in a series of poly-substituted cyclohexanes is the isomer with the greatest number of equatorial substituents. In this connection, we may also mention another general rule (Barton [3]): In a series of poly-substituted cyclohexanes having unlike substituents, the most stable isomer is the one in which the largest substituent is located equatorially.

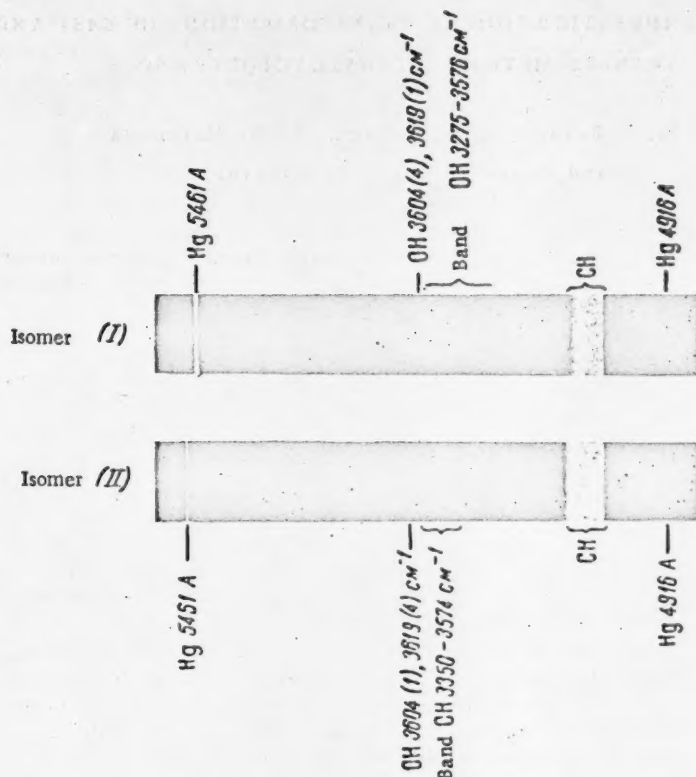
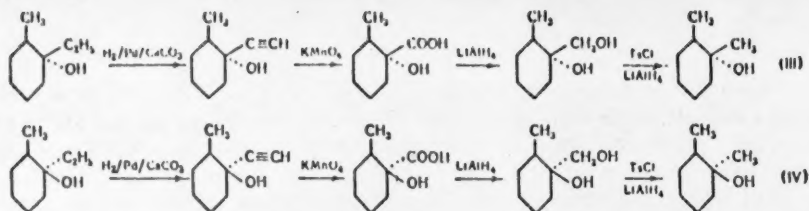


Fig. 1. Raman spectra of cis- and trans-2-methyl-1-ethylcyclohexanols in the frequency region of the hydroxyl group.

2. In the thirties, Chiurdoglu [8] identified the cis- and trans-isomers of a series of substituted cyclohexanols, among them cis- and trans-1,2-dimethylcyclohexanols; however, he did this without discrimination of conformations among them. Two of us [9] synthesized cis- and trans-2-methyl-1-ethylcyclohexanols, (I) and (II).^{*} They were characterized by their physicochemical properties, and also were converted to the known pair [8] cis- and trans-1,2-dimethylcyclohexanols (III) and (IV) according to:

^{*} The cis- and trans-isomers are determined by the position of the alkyl radicals, which are the largest substituents in this case.



However, it is impossible to ascertain accurately the conformation of these compounds by chemical means. In the present work, this question was investigated by means of Raman spectra.

The spectra were obtained in the liquid phase using a domestic ISP-51 spectrograph with an average camera, with excitation from the 4358-A blue line from a mercury lamp.* Cis-2-methyl-1-ethylcyclohexanol, $\Delta\nu$ cm⁻¹: 105(0), 122(0), 146(2), 175(1*), 194(0*), 210(0), 284(3), 322(3), 343(2), 379(4 b db), 415(0), 451(4), 471(1), 492(5), 537(2), 572(1), 605(1), 682(7*), 693(4*), 707(2*), 718(0), 740(0), 759(0), 779(2), 802(3), 822(2*), 836(4*), 862(4), 885(3), 905(1), 921(0), 937(4), 984(6*), 992(2*), 1015(6), 1045(5), 1067(5), 1096(6), 1122(1 b), 1153(6*) - 1168(6*) band, 1230(1), 1263(6), 1308(2), 1345(3 b db), 1443(9**), 1466(8**), 2650(1*), 2681(1*), 2713(1**), 2737(1**), 2852(6*), 2866(6*), 2886(3*), 2902(3*), 2915(3*), 2936(10*), 2945(10*), 2957(4*), 2974(4*), 3122(2), 3183(2 bands), 3275 - 3576, (3 bands), 3594(1), 3604(4), 3619(1), 3636(1).

Trans-2-methyl-1-ethylcyclohexanol, $\Delta\nu$ cm⁻¹: 84(0), 109(0), 121(0), 185(0), 212(0), 249(1), 280(1), 312(1), 365(0), 400(4), 434(5), 451(6*), 468(4*), 497(4), 525(0), 555(5), 586(4), 610(0), 634(1), 662(0), 683(6*), 693(8*), 705(3*), 807(3), 831(6), 865(5), 890(3), 913(3), 945(3*), 961(7*), 973(7*), 994(5), 1020(6), 1046(5), 1077(3*), 1091(7* b), 1146(3**), 1171(7 b**), 1209(3*), 1223(3*), 1263(7** db), 1292(3**), 1305(3**), 1339(5*), 1353(5*), 1445(9**), 1465(8**), 2652(1**), 2679(1**), 2731(1*), 2772(1*), 2845(6**), 2863(6**), 2873(4**), 2892(4**), 2906(4**), 2927(10**), 2944(10**), 2957(4*), 2976(2*), 3088(3), 3157(3 b, bands), 3350-3574 (4 bands), 3581(1), 3604(1*), 3619(4*), 3662(1).

In addition, spectra were taken of 10% (by volume) solutions of these substances in carbon tetrachloride.

3. In considering the spectral data obtained, we will base our discussion on the following experimentally-based conditions.

a) As we have established [10, 11], the effects of neighboring atoms in a molecule (halides, oxygen, secondary and tertiary carbon atoms, etc.) on C-H and O-H bonds are opposed:** the first are electroneutralized (the interatomic distance is decreased, the bond energy and vibrational frequency are increased), and the O-H bond is protonized (the interatomic distance is increased, the bond energy is decreased, and the vibrational frequency is lowered):

	O-H (cm ⁻¹)	High frequency end of the C-H vibrational frequencies (cm ⁻¹)
Primary butyl alcohol	3632	2962
Secondary butyl alcohol	3622	2972
Tertiary butyl alcohol	3615	2978

* Intensity notation: b) broad line; s) sharp line, db) double line; asterisks denote lines in the background which are common with neighboring lines marked with the same number of asterisks.

** In the cited works, we explained the factors which determine this contrary effect.

The directions of the changes in frequencies of the bonds O-H and C-Cl, O-H and C-O, etc. in the corresponding cases are also reversed.

b) The effect of the ring on the frequency of bonds in the ring is, as is well known, especially significant in strained cyclic systems, for example, in cyclopropane. It is decreased in cyclohexane, but is still substantial. This is apparent, for example, at the high-frequency end of the vibrational frequencies of the C-H bonds of methylene groups, which are significantly higher for cyclohexane than for the normal paraffins: n-paraffins, 2908; cyclopropane, 3080; cyclopentane, 2969; cyclohexane, 2941 cm^{-1} [10, 12, 13]. The ring exerts an effect on C-O, C-D, C-Cl, and others. That the vibrational frequencies of the indicated bonds are higher for an equatorial location of the bonds than for an axial location is generally considered, at present, to have an experimental basis (method of infrared spectroscopy) [3, 14-18].

c) In conformity with points a) and b), it can be concluded that an equatorial hydroxyl must be more protonized than an axial hydroxyl (i.e., has lower frequency and bond energy, greater interatomic distance).

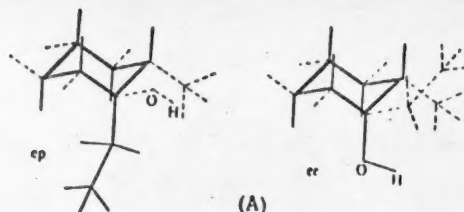
d) The pulse frequency of trans-ortho-substituted cyclohexanes (and also of cyclopentanes and cyclobutanes), as a rule, is higher than the corresponding cis-ortho-substituted compounds [12, 13]. According to the above, the data for trans-isomers belong to ee conformations, and the data for cis-isomers - to ep conformations.

4. In the liquid phase, cis- and trans-2-methyl-1-ethylcyclohexanols (I) and (II) form intermolecular hydrogen bonds. It is clearly apparent in the spectra as a diffusion of the hydroxyl group frequency in the band at the long-wave-length side of the spectrum; this is especially true for I, which indicates, apparently, the more acid nature of this hydroxyl (see Fig. 1) and the frequencies of the spectra presented above). From the high-frequency side of these bands, there is observed a broadened line, which is a combination of frequencies lying close to one another. The diffuse bands disappear in the spectra of solutions of these substances, since the intermolecular hydrogen bonds are broken in these solutions; the lines from the high frequency side of these bands are retained; they belong to the monomer (in the liquid phase, not all molecules of isomers I and II are involved in a hydrogen bond). The most intense of the lines in the spectrum of isomer I is 3604, and for II it is 3619 cm^{-1} . The presence of each of the two mentioned frequencies with a weakened intensity in the spectrum of the other isomer indicates either a small admixture of the epimer or a state of specific dynamic equilibrium in which these epimers are found. The other frequencies bordering on these lines are either traces of rotational-vibrational spectra (see below) or are traces of other conformations present in the mixture in insignificant amount. Since the O-H frequency, in contrast to the frequencies of C-O, C-Cl, C-D, and other bonds, must be higher for axial hydroxyls than for equatorial (see above), the C-OH bond must be equatorial in isomer I for which the hydroxyl group frequency is 3604 cm^{-1} , while it must be axial in isomer II for which the hydroxyl group frequency is 3619 cm^{-1} .

5. The pulse frequency in the spectra of epimers I and II, both in the liquid state and in solution, is also a triplet, not a singlet. The most intense frequency for isomer I is 682 cm^{-1} and for isomer II - 693 cm^{-1} . According to the data presented above, the second frequency relates to the trans-isomer, and the first to the cis-isomer. These frequencies are retained in the spectra of the solutions. Each of these is found with weakened intensity in the spectrum of the other substance, similarly to the corresponding frequencies of the hydroxyl group and for the same reasons (see above). The presence in the spectra of both isomers of the weak frequency 705 cm^{-1} indicates probable admixture in an insignificant amount of other conformations. Since, as we have seen, in I, which is the cis-isomer, the C-OH bond is equatorial and in II, which is the trans-isomer, it is axial, the first isomer is the ep epimer and the second is the ee epimer (more precisely, this is their predominant conformations; there are apparently admixtures of others).

6. This is confirmed (in agreement with the statements under point b above) also by data on the frequencies of the C-O bonds: in the spectrum of isomer I, the system of frequencies in the region relating to vibrations of the C-O bond is shifted to the short-wave side in comparison with the spectrum of isomer II;

II	961 (7)	973 (7)	994 (5)	1020 (6)	1046 (5)
I		984 (6)	1015 (6)	1045 (5)	1067 (5)



7. In isomers I and II, the constituent parts of the molecules (the ethyl and methyl radicals, the hydroxyl group) have free rotation around single bonds; in the hydrogen bond complex which is formed, parts of it can rotate about the C—O bonds (inside the complexes). This rotational (free or hindered) motion of the individual parts of the molecule and complex is, apparently, the source of conversion transformations in the compounds under consideration and of the appearance in the mixture, in addition to the observed basic conformations, of insignificant amounts of other conformations, among them unstable boat forms with a pulse frequency apparently above 802 cm^{-1} [19].

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COMPARATIVE STUDY OF ORDER ARISING IN POLYMERS DURING CRYSTALLIZATION OR ORIENTATION OF MOLECULAR CHAINS

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The structure of linear polymer molecules, consisting of identical, more or less regularly disposed molecular groupings, separate polymer systems in a special group. In distinction to low molecular weight compounds, in which the basic source of order is the spatial disposition of the atomic groupings of the substance examined, a high degree of order in polymeric systems can apparently result from the relative disposition of the linear polymer molecules. As a consequence of this, order in polymeric substances can be attained not only by crystallization of the polymer, but also by relative orientation of the linear molecules irrespective of whether crystallization is present or absent during the process. If, in considering the degree

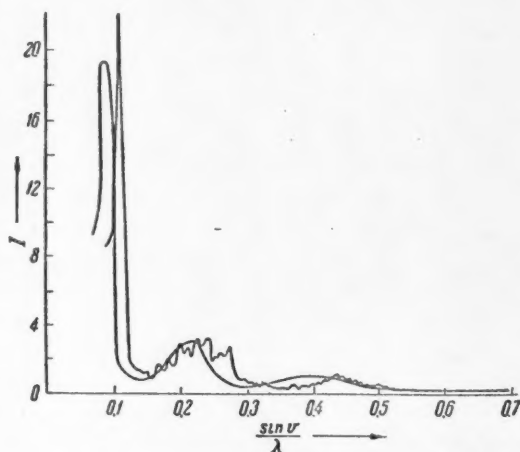


Fig. 1. Curves showing the distribution of intensity with respect to angles for crystalline and amorphous polychlorotrifluoroethylene.

of crystallinity of a polymer, conclusions are based only on a consideration of the geometry of the orderliness of the sample, it is possible to commit an error which has been unfortunately widespread up to the present time, as when clear diffraction patterns obtained for a number of plant fibers were explained by a number of authors as certainly being due to the crystalline state of the polymer. In our opinion, it is necessary to discriminate between the elements of order created by the relative disposition of the chains and order arising from crystallization. This can be confirmed by two routes: by investigating crystallizable polymers by direct structural methods at temperatures above and below the melting points of the crystalline polymers, or by examining the structure of

highly oriented samples while maintaining unchanged the orientation of the investigated polymer during melting and crystallization.

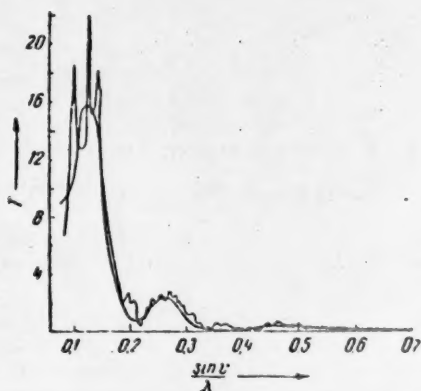


Fig. 2. Curves showing the distribution of intensity with respect to angles for crystalline and amorphous dacron.

An investigation of crystalline polymers at temperatures above and below the melting points of the crystals was carried out by us together with Ermolina using dacron and polychlorotrifluoroethylene. The electron diffraction method was used in this investigation, and it was shown that the interference patterns obtained from samples at temperatures above and below the crystalline melting points have much in common. A comparison of the basic maxima on curves of the distribution of the intensity of coherent diffraction with respect to the angles for both polymers makes it possible to consider that the polymers investigated by us are ordered systems in the amorphous state. Indeed, during plotting of the radial distribution curves we observed that the first maxima on the curves correspond to the distances between atoms in the polymer molecules, and are a consequence of a regular structure of the linear molecules. Subsequent maxima for both of the polymers investigated corresponded to the relative disposition of the polymer molecules (Figs. 1 and 2).

Thus, in the two polymers investigated by us it was noted that their degree of order in the amorphous state is close to that for the crystalline state, differing only in that in the latter case there are additional elements of order. It is evident that emergence of order through the relative disposition of the chains in the polymer proceeds even in the amorphous state. In the process of crystallization, additional bonds arise without a substantial change of order in the disposition of the polymer chains.

It is considerably more difficult to carry out experiments in which a comparative structural investigation is made of oriented polymers which occur both in amorphous and in crystalline states while retaining during the change in state a single degree of orientation. In this case, it is necessary to prevent flow of the polymer at high temperatures by creating a sparse, but stable, structural network and to orient the polymer at a comparatively low temperature at which the polymer possesses comparatively high tear strength so that a considerable force for orientation of the polymer chains can be applied. Then the oriented sample must be held and heated to the crystalline melting point without tearing of the sample due to strains arising in it.

The present investigation was devoted to a comparative study of the order arising in polymers during orientation of the molecular chains. In arranging the work, we were interested in finding the conditions under which the same sample of polymer could retain orientation of the polymer chains unchanged during phase changes of the polymer.

EXPERIMENTAL METHODS

A comparison of the elements of order arising during crystallization of a polymer and during orientation of the molecular chains was carried out by us by applying direct structural methods to polyethylene and gutta-percha. X-ray photographs were obtained using copper $K\alpha$ radiation at 38 kv and 14 ma; electron diffraction patterns were obtained with an EM-4 electron diffraction camera at 40 kv.



Fig. 3. Electron diffraction patterns of a sample of oriented polyethylene: a) before irradiation; b) after irradiation.

Films of low-pressure polyethylene with a thickness of 100-150 μ were obtained by hot pressing. Strips having a width not greater than 3 mm were subjected to limited stretching and irradiated with fast electrons by means of a linear accelerator at 200 kv and a current strength of 20 μ a. Polyethylene films having a thickness of 0.01-0.05 μ , obtained from a hot xylene solution on the surface of hot glycerin, were stretched in special frames and irradiated with fast electrons under vacuum either by means of the linear accelerator or directly in the electron diffraction camera.

The required irradiation dose was controlled by simultaneously irradiating unstretched and stretched samples until amorphization of the unstretched polyethylene films was complete. It was established that during the process of irradiating the unstretched polyethylene films or the stretched films, the ends of which were not held during the irradiation, destruction of the crystals occurred and irreversible amorphization processes occurred in the polymer. During irradiation of stretched samples with a fixed degree of stretching, the interference patterns were characterized by retention of a series of reflections. In Fig. 3 are presented electron diffraction patterns obtained with stretched polyethylene films, both the initial films and after irradiation with fast electrons. A similarity of the interference patterns with respect to a series of reflections was established for polyethylene samples in both the crystalline and the amorphous states. Thus, it was possible to separate the reflections of the interference pattern arising as a result of orientation of the polymer chains, and to determine what part of the pattern was due to simple uniaxial orientation of the linear molecules of the polymer and what fraction arose from the more strict ordering during crystallization.

In addition, we carried out experiments with gutta-percha samples. Thin films of gutta-percha (0.02 to 0.05 μ thickness) were obtained from solution in a gasoline-benzene mixture on a water surface. The films were drawn in special frames, and were vulcanized at room temperature in sulfur monochloride vapors for 2 to 5 minutes in order to create a sparse, but stable, network which prevented flow of the polymer chains at high temperature.

The films were then elongated approximately 150%, transferred to diaphragms with a collodion backing, and heated directly in the electron diffraction chamber to temperatures exceeding the crystalline melting point. In Fig. 4 are presented electron diffraction patterns obtained on stretched, vulcanized gutta-percha films at 20 and 70°. The interference patterns from the melted samples of gutta-percha retained a number of reflections. This interference pattern is a consequence of orientation of the gutta-percha linear molecules.

On the basis of the experimental material obtained, it is our opinion that it has been reliably shown that relative order of polymer molecules can arise even when the polymer is in the amorphous state. This ordered state is apparently a necessary, though insufficient, condition for subsequent crystallization.

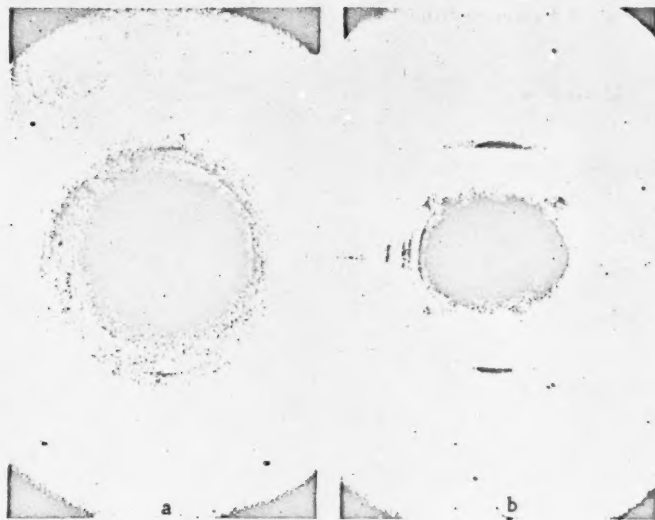


Fig. 4. Electron diffraction patterns of a sample of oriented vulcanized gutta-percha: a) at 20°; b) at 70°.

Moreover, the experimental data obtained confirm that it is possible to separate the order arising in a polymer during orientation of the polymer molecules from that arising during crystallization. During crystallization of polymers, additional order arises in the system, but part of it is small in comparison with the degree of order in oriented samples.

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CYCLIZATION OF 3-ETHYLPENTANE TO ETHYLCYCLOPENTANE

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Recently, we published several papers in which it was reported that paraffinic hydrocarbons can be cyclized in the presence of platinum with the formation of a five-membered ring. This was first shown [1, 2] by means of Raman spectra for *n*-pentane, *n*-octane, and isooctane (2,2,4-trimethylpentane). Later on, the cyclization of isooctane was studied in greater detail [3]; a rather large amount of the hydrocarbon was subjected to contact with the catalyst in order to obtain sufficient product for effective fractional distillation. As a result of this distillation, the cyclization product of isooctane, 1,1,3-trimethylcyclopentane, was isolated in a pure form. In this way it was entirely reliably demonstrated that the direct formation of cyclopentanes from paraffins is possible.

It seemed to us important to investigate, for the sake of comparison, some other hydrocarbons not so highly branched as isooctane. Naturally, it was desirable that this hydrocarbon, like isooctane, yield only a single cyclization product boiling sufficiently far from the original hydrocarbon. Again, this would permit isolation of the cyclization product in a pure form.

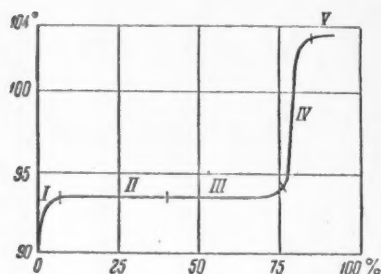


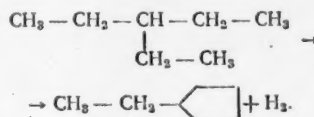
Fig. 1. Catalyzate distillation curve.

The feed hydrocarbon was given a single pass over the catalyst at 310° and a space rate of 0.19-0.22 hour⁻¹. Five portions of hydrocarbon totalling 215.7 g were passed over the catalyst, the catalyzates from each portion being collected separately. Owing to the limited amount of hydrocarbon at our disposal, the last two portions consisted of unreacted 3-ethylpentane separated from the first three catalyzates by distillation in a column.

Analysis of the catalyzates showed that they contained 1.2-1.9% olefins and 0.4-0.7% aromatic hydrocarbons. After the removal of these reaction products by means of chromatography, the content of ethylcyclopentane in the catalyzates (12.5-5.7%) could be determined from the physical constants; the content decreased from experiment to experiment.

By distillation of the combined dearomatized catalyzate we were able to isolate pure ethylcyclopentane, as may be seen from the distillation curve presented in Fig. 1. The constants of Fraction V from this distillation were practically the same as those of ethylcyclopentane.

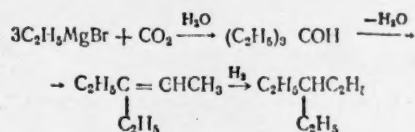
As such a material was selected 3-ethylpentane, which has only one side chain and can give on cyclization a single reaction product - ethylcyclopentane:



The difference between the boiling points of these two hydrocarbons is 10°, and consequently their separation in an efficient column is not attended by any great difficulty.

EXPERIMENTAL METHODS

3-Ethylpentane was prepared from ethylmagnesium bromide and carbon dioxide through triethylcarbinol and 3-ethyl-2-pentene in accordance with the method previously developed by us [4]:



After careful purification by distillation in a column equivalent to 100 theoretical plates and chromatographing over silica gel, the 3-ethylpentane had the following constants: b. p. 93.4°/760 mm, n_D^{20} 1.3934, d_4^{20} 0.6982, which do not differ essentially from the constants of this hydrocarbon according to the most reliable literature data [5]: b. p. 93.475°/760 mm, n_D^{20} 1.39339, d_4^{20} 0.69816.

As in the preceding work, the catalyst was platinized carbon (20% Pt) prepared according to Zelinsky. When the reaction was carried out at 300° and a space rate of 0.9-1.0, this catalyst converted cyclohexane to benzene in yields of 87-92%.

Over a period of three days, three portions of 3-ethylpentane were passed over this catalyst at 310° and a space rate of 0.19-0.22 hour⁻¹. In all, 129.9 g of hydrocarbon was fed, and three catalyzates were collected, the yields and properties of which are shown in Table 1 (Experiments 1-3). After determination of the physical constants and bromine numbers, the catalyzates were chromatographed over silica gel to remove olefins and aromatics. The properties of the catalyzates after chromatization are also presented in Table 1. The content of unsaturates was found by bromine number, and the content of aromatics was determined from the differences in the refractive indices of the catalyzates before and after chromatographing (with correction for unsaturates), which, for such small concentrations of these hydrocarbons, is apparently the most accurate method. The yield of cyclopentanes was also established by refractometry on the basis that the refractive indices of paraffins and naphthenic hydrocarbons are additive in binary mixtures.

TABLE 1
Yields and Properties of Products from the Cyclization of 3-Ethylpentane

Expt. No.	3-Ethylpentane fed, g	Catalyzates and their properties					Properties of catalyzates after chromatization			Ethylcyclopentane content, %
		Wt. g	n_D^{20}	d_4^{20}	unsaturates, %	aromatics, %	n_D^{20}	d_4^{20}	aniline point, °C	
1	34.7	31.7	1.3973	0.7077	1.2	0.7	1.3967	0.7066	62.6	12.5
2	34.7	32.1	1.3971	0.7070	1.7	0.7	1.3964	0.7057	63.0	11.4
3	50.5	—	1.3960	0.7041	1.9	0.4	1.3956	0.7042	63.8	8.3
4	59.0	56.4	1.3958	—	—	—	1.3950	0.7024	—	6.1
5	36.8	35.1	1.3954	—	—	—	1.3949	—	—	5.7

The combined chromatographed catalyzates (89.4 g) were distilled in a column having an effectiveness of 100 theoretical plates. After taking off a small amount of front ends (b. p. 80.7-93.2°/760 mm, n_D^{20} 1.3925, d_4^{20} 0.6977, aniline point 64.4°, weight 5.6 g) 86 ml (59 g) of material with n_D^{20} 1.3932 was collected. This fraction was passed over the same catalyst (see Table 1, Experiment 4), and the catalyzate, after chromatographing and determination of the physical constants, was added to the residue from the preceding distillation.

Again the recovered 3-ethylpentane fraction, weighing 36.8 g was passed under the same conditions over the same catalyst (see Table 1, Experiment 5), and, after chromatographing and determination of the physical constants, it was added to the residue from the preceding distillation. The thus obtained concentrate, weighing 63.3 g was carefully distilled in the same column. The results of this distillation are shown in Fig. 1 and Table 2.

TABLE 2
Results of the Distillation of the Catalyzate

Fraction No.	Boiling range, °C at 760 mm	Yield fraction		n_D^{20}	d_4^{20}	Content cyclopentane hydrocarbons, in %	
		in g	in %			in the fraction	in deaeromatized catalyzate
I	90.6-93.3	4.2	6.5	1.3925	0.6977	10-15	0.6-0.9
II	93.3-93.5	24.1	37.3	1.3934	—	—	—
III	93.5-94.1	17.5	27.1	1.2934	—	—	—
IV	94.1-103.35	6.2	9.5	1.4055	0.7299	51	4.7
V	103.35-103.5	4.9	7.5	1.4196	0.7657	99	7.4
Residue	—	7.7	11.9	1.4195	—	99	11.8
Total		6.46					

As may be seen from Table 2, Fraction V had physical constants very close to the most reliable data for ethylcyclopentane [5]: b. p. 103.466°/760 mm; n_D^{20} 1.41951, d_4^{20} 0.76647.

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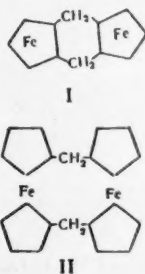
DETERMINATION OF THE LOCATION OF SUBSTITUENTS IN FERROCENE COMPOUNDS BY INFRARED ABSORPTION SPECTRA

Academician A. N. Nesmeyanov, L. A. Kazitsyna,

B. V. Lokshin, and I. I. Kritskaya

Up to the present, several communications have been published on the infrared spectra of ferrocene and its derivatives [1-8]. Apparently, the largest set of infrared spectra of substances of this series is the set composed of the spectra described by one of us and co-workers [9-16]. A comparison of these data permitted us to arrive at certain conclusions as to correlations between the infrared spectra of ferrocene derivatives and certain traits of their structure, conclusions which form the subject of this communication. These conclusions appeared to us to constitute an important method for establishing the structures of ferrocene homologs obtained by the direct alkylation of ferrocene by Friedel-Crafts synthesis. Moreover, they permitted more accurate definition of the structure of products obtained by one of us and Kritskaya [16] by the condensation of formaldehyde and other aldehydes with ferrocene; these products contain two ferrocene rings connected by two methylene groups (corresponding to benzyldiene groups).

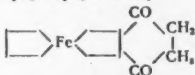
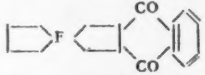
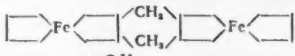
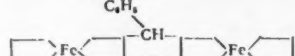
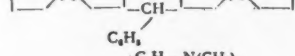
Recently, one of us and E. G. Perevalova and co-workers [17] developed two chemical methods for establishing the location of substituents in ferrocene derivatives, each of which has its limitations. The first (catalytic hydrogenation under severe conditions) leads to the corresponding cyclopentane derivative. The second (bromination) leads to the formation of pentabromocyclopentane in the case of those ferrocene derivatives which have a single substituted cyclopentadienyl ring. This latter method is identical in the scope of its application to the method substantiated here for establishing the same structural trait by infrared spectra, and the correspondence between these methods is established in the present work. Thus, the products of the condensation of ferrocene with formaldehyde (and other aldehydes) are shown by both methods to have unsubstituted cyclopentadienyl rings and, consequently, the structure shown by Formula I, and not the isomer II.



The infrared spectra of ferrocene compounds, as shown by Lippincott and Nelson [3], are distinguished by simplicity owing to the high symmetry of the molecules and in addition to C-H valence vibrations in the region of 3000-3100 cm⁻¹ there are only four adequately intense bands: the frequencies for ferrocene at 811 and 1001 cm⁻¹ arise as a result of deformation vibrations, the frequency at 1108 cm⁻¹ is an antisymmetric

vibration of the ring, and the frequency at 1411 cm^{-1} is an antisymmetric valence vibration of the C-C bond. The most intense of these bands are at frequencies of 1002 and 1108 cm^{-1} . They were selected by us as criteria of the location of substituents in ferrocene compounds.

TABLE 1

Test No.		ν, cm^{-1}	Source
1	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_5$	1004; 1110	—
2	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{CH}_3$	1004; 1109	(*)
3	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{CH}(\text{CH}_3)_2$	1003; 1107	(*)
4	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{C}(\text{CH}_3)_3$	1000; 1106	(*)
5	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{C}_6\text{H}_5$	1001; 1107	(**)
6	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{COCH}_3$	1005; 1105	(**)
7	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{COOH}$	1006; 1108	(**)
8	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{COOCH}_3$	1005; 1108	(**)
9	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4(\text{CH}_2)_2\text{COOH}$	1002; 1104	(**)
10	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{CO}(\text{CH}_2)_2\text{COOH}$	1006; 1106	(**)
11	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{CO}(\text{CH}_2)_2\text{COOCH}_3$	1000; 1105	(**)
12	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{NHCOCH}_3$	1001; 1104	(**)
13	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{COC}_6\text{H}_4\text{COOH}$	1005; 1105	(**)
14	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{COC}_6\text{H}_4\text{COOCH}_3$	1000-1007; 1104	(**)
15	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{C}_6\text{H}_4\text{NO}_2$	1000; 1106	(**)
16	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{CH}_2$	1002; 1104	—
17	$\text{CH}_3\text{C}_6\text{H}_4\text{FeC}_6\text{H}_4\text{CH}_3$	—	(**)
18	$\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{FeC}_6\text{H}_4\text{C}_6\text{H}_5$	—	(**)
19	$\text{CH}_3\text{OHC}_6\text{H}_4\text{FeC}_6\text{H}_4\text{CH}_2\text{OH}$	—	(**)
20	$\text{CH}_3\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{FeC}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$	—	—
21	$\text{CH}_3\text{COOC}_6\text{H}_4\text{FeC}_6\text{H}_4\text{COOCH}_3$	—	(**)
22	$\text{CH}_3\text{COC}_6\text{H}_4\text{FeC}_6\text{H}_4\text{COOCH}_3$	—	(**)
23	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_4\text{FeC}_6\text{H}_4\text{COOCH}_3$	—	(**)
24		999; 1104	(**)
25		1003; 1107	(**)
26		1005; 1104	(**)
27		1004; 1106	(**)
28		999; 1105	—
29	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4(\text{CH}_3)_2$	1004; 1107	(*)
30	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4(\text{C}_2\text{H}_5)_2$	998; 1107	(*)
31	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4(\text{C}_2\text{H}_5)_2$	998; 1107	(*)
32	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4(\text{CH}_2(\text{CH}_2)_2)_2$	1002; 1107	—
	$\text{C}_6\text{H}_5\text{FeC}_6\text{H}_4(\text{C}(\text{CH}_2)_2)_2$	1000; 1107	—

The spectra were obtained using a single beam IKS-II, i.e., spectrometer, and were recorded on a strip chart by means of an EPP-09 electronic potentiometer. Solid specimens were prepared in the form of pastes in vaseline oil, while liquid specimens were used in the pure form with a cell thickness of 0.05 mm.

We obtained spectra for ferrocene and 15 monosubstituted ferrocenes with substituents of the most varied structures (Table 1, Nos. 1-16).

We also obtained the spectra of 7 disubstituted ferrocene compounds, the substituents of which had previously been shown chemically to be on different rings (Table 1, Nos. 17-23). The frequencies at 1002 and 1107 cm^{-1} were not observed in the spectra of these compounds.

In the spectra of compounds 24-28 (Table 1) were found intense bands with frequencies of 1002 and 1107 cm^{-1} , indicating the presence of a free cyclopentadienyl ring.

For compounds 26, 27, and 28, the presence of a free cyclopentadienyl ring was also confirmed chemically by bromination.

The action of an excess of bromine in carbon tetrachloride at the boiling point of the latter on all three of these compounds gave pentabromocyclopentane with a m. p. of 83-101° (mixture of stereoisomers) [17]. For the product of the condensation of ferrocene with formaldehyde the yield of pentabromocyclopentane was 43% of theoretical calculated on the basis of two unsubstituted cyclopentadienyl rings per molecule. Under these same conditions, the products of the condensations with aromatic aldehydes (27 and 28) decomposed with greater difficulty, and only small yields of pentabromocyclopentane were obtained. It should also be noted that for compound 28 (m. p. 257°), along with the strong characteristic frequency, a frequency at 1350 cm^{-1} was also observed; this frequency is characteristic for deformation vibrations of the hydroxyl group, and confirms the proposed open structure.

The spectra of the disubstituted ferrocenes (29-33, Table 1) contain the frequencies 1002 and 1107 cm^{-1} , which can be considered proof of the presence of a free cyclopentadienyl ring.

Infrared spectra are also available in the literature for 1,2-ferrocenedicarboxylic acid, its ester and anhydride, and these all have frequencies at 1000-1002 and 1102-1116 cm^{-1} [7].

A comparison of two isomeric ethylferrocenes substituted on one ring (n_D^{20} 1.5820 and n_D^{20} 1.5847) showed that their spectra are similar with the exception of a frequency at 1277 cm^{-1} , which appeared only in the spectrum of one of these compounds. Work on the determination of isomers which are disubstituted on one ring continues.

TABLE 2

No. in Table 1	ν carbonyl group, cm^{-1}	No. in Table 1	ν carbonyl group, cm^{-1}
6	1660	22	1657
10	1660	23	1661
11	1670	24	1678
13	1650	25	1657
14	1650		

The frequency of the C=O group was detected for ferrocene compounds containing a carbonyl group conjugated with the ferrocene ring (Table 2).

It is apparent from Table 2 that the frequency of ketonic C=O lies in the region 1650-1678 cm^{-1} , which indicates a significant shift of the C=O frequency with respect to the corresponding aliphatic carbonyl compounds; this shift can be explained by conjugation of the carbonyl group with the cyclopentadienyl ring. This phenomenon is analogous to the shift in the carbonyl frequency from 1710 cm^{-1} in acetone to 1685 cm^{-1} in acetophenone [19] owing to conjugation with the aromatic ring.

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SYNTHESIS OF TETRAKIS [TRIALKYL (ARYL) SILOXY] TITANIUM COMPOUNDS BY TRANSESTERIFICATION OF TETRAALKYL TITANATES

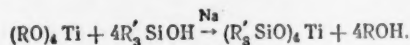
B. N. Dolgov and N. F. Orlov

(Presented by Academician A. N. Nesmeyanov, June 2, 1957)

The only monomeric organosilicotitanium compound of the type $(R_3\text{SiO})_4\text{Ti}$ is tetrakis(trimethylsiloxy) titanium - $[(\text{CH}_3)_3\text{SiO}]_4\text{Ti}$ - which was first obtained, in 18% yield, in 1955 by the reaction of trimethylsilanol with titanium tetrachloride in the presence of ammonia [1] and again in 1957 by the reaction of sodium trimethylsilanolate with titanium tetrachloride [2].

We studied the possibility of synthesizing tetrakis(trialkyl (aryl)siloxy) titanium compounds by a transesterification reaction between alkyl orthotitanates and trialkyl (aryl)silicols in the presence of metallic sodium as a catalyst [3].

The reaction proceeds with good yields according to:



The resulting tetrakis(trialkyl (aryl)siloxy) titanium compounds are colorless crystals or relatively mobile liquids. They are stable in dry air, and are readily soluble in organic solvents.*

The tendency toward hydrolysis decreases with an increase in the size of the radical bonded to the silicon.

EXPERIMENTAL METHODS

Starting reagents. The alkyl orthotitanates were prepared by the method of A. N. Nesmeyanov [4] and had constants in agreement with those in the literature. The trimethylsilanol was prepared by hydrolysis of hexamethyldisilamine [bis(trimethylsilyl)amine] [5]; the remainder of the silanols were prepared by hydrolysis of alkoxy derivatives of acetic acid in the presence of several drops of sulfuric acid. The constants of the silanols were in agreement with the most reliable literature data.

Method of syntheses. All syntheses, with the exception of the synthesis of tetrakis(triphenylsiloxy) titanium, were carried out in a distillation flask fitted with a herringbone dephlegmator. An equimolar mixture of the alkyl orthotitanate and trialkylsilanol was heated in the presence of 0.01% Na until the evolution of alcohol ceased. The residue was fractionated under vacuum. The physical constants, yields, and analyses of the resulting tetrakis(trialkyl (aryl)siloxy) titanium compounds are presented in Table 1.

* Tetrakis(triphenylsiloxy) titanium is very difficultly soluble. It can be recrystallized only from boiling xylene.

Analysis. Determination of silicon was carried out by wet oxidation of the material with a mixture of oleum and nitric acid. The residue of silicic acid was filtered and calcined at 900°. The titanium was determined in the filtrate by precipitation with ammonia. Calcination of this precipitate was also carried out at 900°.

TABLE 1
Tetrakis [Trialkyl (aryl)siloxy] Titanium Compounds

Compound	B. p. °C.	Pressure, mm Hg	M. p. °C.	d_4^{20}	n_D^{20}	Yield, %	Si, %		Ti, %	
							calc.	found	calc.	found
(CH ₃) ₃ SiO ₂ Ti*	114	11	—	0.9038	1.4300	50.0	27.76	27.4	11.84	11.94
(C ₂ H ₅) ₃ CH ₂ SiO ₂ Ti	154	33	—	0.9244	1.4545	90	21.74	21.61; 21.22	9.27	9.55; 9.57
(C ₂ H ₅) ₂ SiO ₂ Ti	195	3.5	99-101	—	—	98	19.61	19.54; 19.67	8.36	8.15; 8.71
(n-C ₄ H ₉) ₃ CH ₂ SiO ₂ Ti	199	3.5	—	0.9056	1.4582	83	17.86	17.60; 17.30	7.61	7.82; 8.04
(C ₆ H ₅) ₃ SiO ₂ Ti	—	—	1480	—	—	85	9.60	9.58; 9.58	4.16	4.40; 4.70

* Literature data [1]: b. p. 106°/7 mm, d_4^{20} = 0.9078, n_D^{20} = 1.4278.

1. **Synthesis of tetrakis(trimethylsiloxy)titanium.** In a flask fitted with a herringbone deflegmator was placed 5 g (0.022 mole) of ethyl orthotitanate, b. p. 140°/6 mm, 13 g (0.145 mole, 65% excess) of trimethylsilanol, b. p. 98.5-100°/760 mm, n_D^{20} = 1.3886, d_4^{20} = 0.8120 and 0.01 g of Na. The mixture was slowly heated until the temperature of the effluent gases reached 100°. Vacuum distillation of the residue yielded 4.5 g (50.5%) of tetrakis(trimethylsiloxy)titanium, b. p. 110°/10 mm, n_D^{20} = 1.4275, d_4^{20} = 0.9004.

2. **Synthesis of tetrakis(methyldiethylsiloxy)titanium.** On heating 14.2 g (0.12 mole) of methyl-diethylsilanol, b. p. 61°/30 mm, n_D^{20} = 1.4204, d_4^{20} = 0.8503 and 6.8 g (0.03 mole) of ethyl orthotitanate in the presence of 0.005 g of sodium, 4.9 g (89%) of ethyl alcohol, b. p. 79-81° was obtained. Vacuum distillation yielded 14.0 g (90.2%) of tetrakis(methyldiethylsiloxy)titanium, b. p. 183-186°/6.5 mm. After a second distillation, the product had the constants given in Table 1.

3. **Synthesis of tetrakis(triethylsiloxy)titanium.** A mixture of 13.0 g (0.1 mole) of triethylsilanol, b. p. 75°/24 mm, n_D^{20} = 1.4340, d_4^{20} = 0.8645, 6.8 g (0.01 mole) of butyl orthotitanate, b. p. 165-167°/4 mm, n_D^{20} = 1.4905, d_4^{20} = 0.998, and 0.001 g of sodium was heated until the temperature of the effluent gases reached 118°. 7 g were distilled during the heating. Vacuum fractionation yielded 10 g (98%) of tetrakis(triethylsiloxy)titanium, b. p. 192-196°/4 mm, m. p. 99-101°.

4. **Synthesis of tetrakis(methyldi-n-propylsiloxy)titanium.** Under similar conditions, from 14.6 g (0.1 mole) of methyl-n-propylsilanol, b. p. 80°/17 mm, n_D^{20} = 1.4275, d_4^{20} = 0.8436, 5.7 g (0.025 mole) of ethyl orthotitanate, and 0.01 g of sodium was obtained 13.0 g (83%) of tetrakis(methyldi-n-propylsiloxy)titanium, b. p. 186-188°/3 mm, n_D^{20} = 1.4570, d_4^{20} = 0.9044.

5. **Synthesis of tetrakis(triphenylsiloxy)titanium.** In a 250 cc flask was placed 11.6 g (0.04 mole) of triphenylsilanol, m. p. 153°, 2.3 g (0.01 mole) of ethyl orthotitanate, 0.01 g of sodium, and 100 ml of benzene. The contents were heated at the boiling point of the solvent for a period of 6 hours. The resulting finely-crystalline precipitate was filtered, 10 g (85%) of tetrakis(triphenylsiloxy)titanium was obtained, which after recrystallization from boiling o-xylene, had a m. p. of approximately 480°.

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CATALYTIC DEHYDROGENATION OF ISOPENTANE

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The use of isopentane, a petroleum hydrocarbon, for expanding the raw material base of the synthetic rubber industry has great significance in the national economy. One of the possible routes for the production of isopentane, an SR (synthetic rubber) monomer, is the catalytic dehydrogenation of isopentane to isoamylenes and dehydrogenation of the latter to isoprene: $C_5H_{12} \rightarrow C_5H_{10} \rightarrow C_5H_8$.

Literature data on the conversion of isopentane to isoamylenes are very scarce; the only published works are those of Shuikin and co-workers on the catalytic dehydrogenation of isopentane [1] and of Mamedaliev and co-workers on the formation of isoamylenes during the catalytic dehydrogenation of gasolines boiling at 27-29° and 27-32° [2]. The description in the foreign patent literature of the catalytic dehydrogenation of isopentane is limited to general statements, and the most frequently recommended catalysts are chrome-alumina catalysts with or without promoters; see, for example [3].

Thus, the study of the catalytic dehydrogenation of isopentane to isoamylenes is still in the initial stage.

Many years of investigation by M. N. Marushkin in the Institute of Organic Chemistry of the Academy of Sciences, USSR resulted, in 1953, in the development of an active chrome-alumina catalyst for the dehydrogenation of n-butane and propane, and this catalyst was used in 1954 for the study of the dehydrogenation of isopentane to isoamylenes. The composition of the catalyst, in mole percent, is: Al_2O_3 88, Cr_2O_3 9; K_2O 3; the bulk density is 1.14 g/cc. The catalyst possessed high mechanical strength toward crushing; spheres 5-6 mm in diameter crushed only under a load of 40-60 kg.

The dehydrogenation of isopentane was carried out in a laboratory flow-type apparatus with a quartz catalyst tube. Fresh or regenerated catalyst (20 cc) was heated to the temperature of the experiment in a stream of air; the latter was then replaced by nitrogen, and isopentane was introduced into the tube. The catalyst was regenerated in a stream of air at the temperature of the experiment for about an hour. Feed for the experiments was petroleum isopentane, which, after distillation in a column of 35 theoretical plates, had a b. p. of 27.8°/760 mm; n_D^{20} 1.3538; d_4^{20} 0.6194. The liquid reaction products were condensed by cooling with solid CO_2 , and the tail gas was collected in a gasometer over brine. Collection of the reaction products was carried out after the catalyst had stabilized, i.e., 5-10 minutes after feeding of the isopentane to the catalyst tube had been started.

Total unsaturation of the condensate was determined bromometrically by the method of Rosenmund [4] and the isoprene content was determined gravimetrically by reaction with maleic anhydride. Gaseous reaction products were analyzed in an Orsat apparatus. The activity and selectivity of the catalyst was calculated as the yield (in weight percent) of unsaturated hydrocarbons with respect to, respectively, isopentane fed and isopentane consumed.

* Deceased.

A study of catalyst operation in short on-stream periods* (30-90 minutes) in the temperature interval 500-575° and at space rates of 0.3 to 4.2 hours⁻¹ showed that its activity increases with an increase in process temperature, reaching a maximum value at 550° (Fig. 1). With an increase in temperature, maximum catalyst activity shifts in the direction of decreasing contact time from 8 to 3 seconds (Fig. 1), the sharpest variation in activity with contact time occurring at 550°. With a change in space rate, catalyst activity remained at practically maximum value in the interval of 0.7 to 2.6 hours⁻¹ (Fig. 2). Under these conditions, the catalyzates obtained at 550° contained up to 58% by weight of unsaturated hydrocarbons; the yields of the latter based on isopentane fed varied in the range 45-49% by weight, while the yields based on isopentane consumed varied from 70 to 90% by weight; catalyzate yield varied from 80 to 95% by weight. Catalyst selectivity (see above) increased with a decrease in contact time; selectivity was practically the same at 525 and 550°, but it decreased at 575° owing to an increase in cracking reactions at this temperature (Table 1).

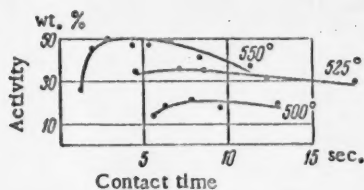


Fig. 1. Effect of contact time on catalyst activity.

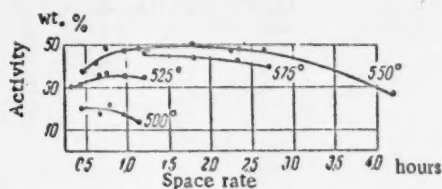


Fig. 2. Effect of space rate on catalyst activity.

Productivity of the catalyst increased sharply with an increase in reaction temperature and isopentane feed rate. The highest catalyst productivity — about 700 g of unsaturates per liter of catalyst per hour — was reached at 550° and a space rate of 2.6 hours⁻¹. Catalyst productivity decreased at 575° (Fig. 3).

TABLE 1

Space rate, hours ⁻¹	Contact time, sec.	Catalyst selectivity, wt. %		
		at 525°	at 550°	at 575°
0.45	11-12	56	53	—
0.64	8	70	60	—
0.76	7	74	78	—
0.96	5-6	78	72	—
1.20	4	78	80	71
1.80	3	—	85	72
2.66	2	—	89	73
4.17	1	—	80	—

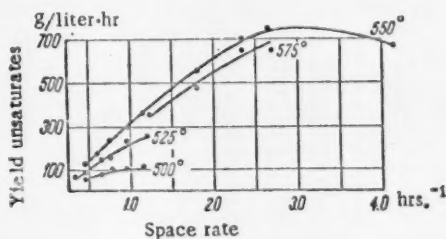


Fig. 3. Catalyst productivity.

Thus, the optimum reaction temperature must be 550°. All further investigation of the operating qualities of the catalyst was carried out at this temperature; catalyst stability and extent of poisoning were determined, and the most efficient on-stream time for productivity was determined. In order to obtain comparable results, all experiments were carried out at a space rate of 1.2 hours⁻¹.

It was shown that the average activity (productivity) of the catalyst per cycle decreases linearly with an increase in cycle length (Fig. 4). The highest catalyst activity was obtained at an on-stream time of one hour. It also follows from Fig. 4 that catalyst selectivity does not depend on the extent of poisoning.

* By on-stream period is meant the period of catalyst operation between two regenerations.

With a continuous on-stream period, without catalyst regeneration, of more than 8 hours (550°, 1.2 hours⁻¹ space rate), the extent of isopentane dehydrogenation decreased by almost a factor of 3 (from 46 to 17 wt. %) for the first 4 hours, and then showed practically no further change. After regeneration, the catalyst completely recovered its initial activity. This poisoning is evidently connected with coking of the catalyst in the dehydrogenation process. Deposition of "coke" on the catalyst proceeds to a greater extent in the first hour of operation than in succeeding hours. Under the conditions investigated, 3.9 wt. % "coke" had formed on the catalyst at the end of the first hour, and after three hours of catalyst operation without regeneration only 6.3 wt. % had formed.

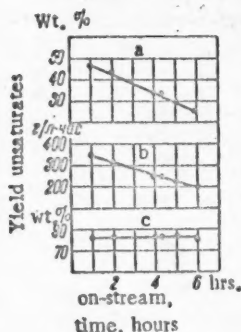


Fig. 4. Effect of on-stream time on catalyst operation (550°, space rate 1.2 hours⁻¹): a) catalyst activity, b) productivity, c) selectivity.

content of saturated hydrocarbons varied from 9 to 26 vol. % as the reaction temperature was increased from 500 to 550° and the isopentane feed rate decreased from 1.2 to 0.5 hours⁻¹. The concentration of unsaturated hydrocarbons in the tail gas was very small and comprised about 1 vol. % over the entire temperature and space-rate intervals studied. The results of the gas analysis indicate that cracking reactions occurring during isopentane dehydrogenation increase with an increase in process temperature or a decrease in space rate, as would be expected.

With periodic regeneration, the activity of the catalyst did not change over the course of 45 cycles with one-hour on-stream periods (550°, space rate 1.2 hours⁻¹). Under these conditions, the yield of catalyzate averaged 90 wt. %, and the total unsaturates content was 52 wt. %; the yield based on isopentane fed was 47-49% wt. % for isoamylenes and about 2 wt. % for isoprene; selectivity for dehydrogenation of isopentane to isoamylenes averaged 78 wt. %. The data cited attest to the high stability of the catalyst, which is in agreement with the results from the dehydrogenation of n-butane to butylenes over this same catalyst - its activity was almost unchanged after 220 one-hour working cycles.

In the isopentane dehydrogenation process, gaseous products are formed, the composition of which is determined by the reaction temperature and the space rate. The tail gas consisted mainly of hydrogen (70-90 vol. %); the con-

TABLE 2

20-38° Fraction	Unsaturated components in catalyzate, wt. %		
	at 500°	at 525°	at 550°
Total unsaturation *	18.6	41.6	52.2
Isoprene **	0.4	1.5	4.2
2-Methyl-2-butene	10	15	20/25***
2-Methyl-1-butene	5	15	15/30***
3-Methyl-1-butene	3	3	5/35***

* Determined by Rosenmund method.

** Determined by weight increase of maleic anhydride.

*** Second figure obtained by analysis of a 20-38° fraction not treated with maleic anhydride.

For the investigation of the composition of the catalyzates obtained at various space rates in the range 500-550°, the catalyzates were first freed from the gaseous fraction (b. p. to 20°) and the products boiling above 38°. All catalyzates investigated boiled in the range 20-170°, the 20-38° fraction comprising about

90 wt. % of the total amount and the 38-170° fraction comprising about 9%. The 20-38° fraction was treated with maleic anhydride to remove the dienes, again distilled, and investigated by means of Raman spectra. In Table 2 are presented the results of the determinations of unsaturated components in the 20-38° C fraction of the catalyzates.

With an increase in reaction temperature from 500 to 550°, the total content of unsaturates in the catalyzate increased almost by a factor of 3; the isoprene concentration increased by a factor of 10, that of 2-methyl-2-butene by a factor of 2, and that of 2-methyl-1-butene by a factor of 3, while the content of 3-methyl-1-butene was almost unchanged. The predominant products of the catalytic dehydrogenation of isopentane in the temperature interval 500-550° are 2-methyl-2-butene and 2-methyl-1-butene; 3-methyl-1-butene and isoprene are present in the catalyzate only in small amounts.

The data presented in Table 2 show that care is required in using Raman spectra for the analysis of the products of the catalytic dehydrogenation of isopentane. In case isoprene is present in the reaction products, the most intense lines for it and 3-methyl-1-butene, which are very close together, are superimposed. Moreover, the isoprene line at 1640 cm^{-1} is approximately 12 times more intense than the 3-methyl-1-butene line at 1642 cm^{-1} , and, therefore, with even a small content of isoprene (4%) the line at 1640 cm^{-1} maximizes not only the 3-methyl-1-butene line at 1642 cm^{-1} but also the 2-methyl-1-butene line at 1651 cm^{-1} , which leads during analysis to sharply increased results for the latter two.

The Raman spectra of the catalyzate fractions from the dehydrogenation of isopentane were studied in the Commission for Spectroscopy of the Academy of Sciences, USSR by V. T. Aleksanyan and Kh. E. Sterin, to whom we express our gratitude for aid in the investigation of the catalyzates.

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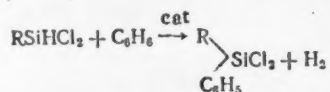
* Original Russian pagination. See C. B. Translation.

ON THE CATALYTIC PHENYLATION OF HYDROGEN-CONTAINING ALKYLCHLOROSILANES WITH BENZENE

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(Presented by Academician B. A. Kazansky, June 28, 1957)

There is little data in the literature on the catalytic reaction of hydrogen-containing alkylchlorosilanes and of trichlorosilane with aromatic hydrocarbons



The available, brief patents mention chiefly the interaction of trichlorosilane with benzene in the presence of aluminum chloride [1, 2], boron trifluoride [3, 4], boron trichloride [5, 3], boric acid [3], and compounds containing both boron and silicon [3].

According to the data of one patent [6], the phenylation of methyldichlorosilane with benzene should be carried out in an autoclave at 300° for 16 hours. This procedure gave methylphenyldichlorosilane in a yield of 6.2% of theoretical calculated on the methyldichlorosilane, and also phenyltrichlorosilane, dimethyldichlorosilane, and tetrachlorodimethylphenylenedisilane [bis(methyldichlorosilyl)benzene].

In a brief report [7], E. A. Chernyshev and A. D. Petrov indicated that it is possible to obtain methylphenyldichlorosilane in the presence of Raney nickel with a yield of 17.7% based on the methyldichlorosilane reacted; it was also mentioned that in the presence of AlCl_3 the yield of methylphenyldichlorosilane is 23%.

The fact that, with the exception of Raney nickel, the catalysts are all compounds of the elements of Group III of the periodic system attracts one's attention.

We have carried out an investigation of the phenylation of methyl- and ethyldichlorosilanes with benzene.

Experimental testing showed that ferric chloride, barium chloride, benzoyl peroxide, and freshly prepared boric anhydride have no catalytic effect on this reaction. Further investigation by us was carried out with boric acid, which is a quite active and satisfactory catalyst. The experiments were carried out in a 100 ml autoclave, which was half filled with a mixture of alkylchlorosilane and benzene to which the boric acid was added.

It was established that in the presence of 1-2% boric acid, based on the weight of the mixture, phenyltrichlorosilane was also formed, the separation of which from the methylphenyldichlorosilane by rectification was practically impossible (the difference in boiling points is about 2°). A decrease in the amount of catalyst to 0.1% made possible the practically complete elimination of the formation of phenyltrichlorosilane.

Depending on the temperature, the pressure rise in the autoclave, which occurred chiefly owing to the liberation of hydrogen during the phenylation process, ceased after 1 hour (at 290°) or 2 hours (at 250°). Lengthy

heating, which is recommended in the patents [2-4, 6], is unfavorable, since it causes a decrease in the yield of the of the desired product owing to its further conversion.

The optimum synthesis temperature in the presence of 0.1% boric acid is close to 240°. Lowering the temperature by 5-10° sharply slows down the reaction. A significant increase in the synthesis temperature leads to a decrease in the yield of alkylphenyldichlorosilanes and to the formation of difficultly separable by-products, mainly phenyltrichlorosilane. This last is easily judged by the increase in the density of the separated methylphenyldichlorosilane fraction (see Table 1 in which is shown the variation in yield of methylphenyldichlorosilane with synthesis temperature). The duration of heating at the indicated temperatures was 2 hours; the molar ratio $\text{CH}_3\text{SiHCl}_2:\text{C}_6\text{H}_6$ was 1:1.2, the amount of boric acid was 0.1% of the weight of the mixture.

TABLE 1

Synthesis temperature, °C	Maximum pressure at synthesis temp. atm.	Residual pressure at 20°, atm.	Yield of $\text{CH}_3\text{C}_6\text{H}_4\text{SiCl}_2$ based on $\text{CH}_3\text{SiHCl}_2$		$\text{CH}_3\text{SiHCl}_2$ recovered, %	d_4^{20} of desired fraction
			% of that charged	% of that reacted		
240	70	31	16.8	29.6	42.8	1.1778
250	100	49	13.6	14.8	13.7	1.1772
290	122	49	6.2	6.6	9.8	1.1846

The comparatively low yields of alkylphenyldichlorosilane was chiefly due to the high reactivity of the alkyldichlorosilanes, which, under synthesis conditions, are capable of undergoing not only phenylation but also various other reactions. Among these conversions should be noted thermal rearrangements, condensation, and reaction with the alkylphenyldichlorosilane. Therefore, it was natural to suppose that a decrease in the fraction of alkyldichlorosilane in the reaction mixture and an increase in the fraction of benzene would bring about an increase in the yield of alkylphenyldichlorosilane. Results, presented in Table 2, of experiments at different methyldichlorosilane-to-benzene ratios confirm, within the range investigated, the above supposition. The experiments were carried out at 240° and with the addition of 0.1% boric acid.

TABLE 2

Molar ratio $\text{CH}_3\text{SiHCl}_2:\text{C}_6\text{H}_6$	Maximum pressure at synthesis temp. atm.	Residual pressure at 20° atm.	Time required for attainment of constant pressure	Yield of $\text{CH}_3\text{C}_6\text{H}_4\text{SiCl}_2$ based on $\text{CH}_3\text{SiHCl}_2$	
				% of that charged	% of that reacted
1:1.2	100	38	1 hr. 45 min.	13.4	17.7
1:3	80	29	2 hrs.	23.4	32.5
1:5	68	25	3 hrs. 30 min.	23.7	-

When the synthesis was carried out in an autoclave of larger volume, the yield of methylphenyldichlorosilane reached 40% of the reacted methyldichlorosilane.

In the mixture after completion of the synthesis process, along with methylphenyldichlorosilane and unconverted methyldichlorosilane and benzene, the following by-products were present: dimethyldichlorosilane and methyltrichlorosilane (in a weight ratio of 1:3), other products of the disproportionation and condensation of methyldichlorosilane, and high-boiling material formed by the further reaction of methylphenyldichlorosilane with methyldichlorosilane.

The gaseous products of the reaction consisted of 90-95% hydrogen and 5-10% hydrocarbons.

The synthesized methylphenyldichlorosilane was twice distilled in a column of 25 theoretical plates, and the resulting material boiled at 203.1°/749 mm; d_4^{20} 1.1778; n_D^{20} 1.5188; $MR_{D\text{found}}$ 49.24; $MR_{D\text{calc}}$ 49.24.

Found %: Cl 37.12. Calculated %: Cl 37.10.

The reaction of benzene with ethyldichlorosilane in the presence of boric acid proceeded in a similar manner. The optimum synthesis temperature was about 20° higher than in the case of methylchlorosilane — close to 250°. The ethylphenyldichlorosilane isolated had b. p. 225.2°; d_4^{20} 1.1554; n_D^{20} 1.5198; $MR_{D\text{found}}$ 53.96, $MR_{D\text{calc}}$ 53.87.

Found %: Cl 34.60. Calculated %: Cl 34.57.

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TRIPHENYLOXONIUM SALTS

Academician A. N. Nesmeyanov and T. P. Tolstaya

By the decomposition of aryldiazonium fluoborates in a medium of bromobenzene or chlorobenzene we were recently able to obtain for the first time a number of diarylbromonium and diarylchloronium salts [1]. In the present paper, we describe the application of this method to the preparation of the previously unknown tertiary aromatic oxonium salts.

In contrast to the trialkyloxonium salts of Meerwein [2], triphenyloxonium salts are extremely stable compounds with decomposition temperatures above 150°C. All of the salts described in the present paper with the exception of the chloride and bromide are difficultly soluble in water. In contrast to Meerwein's salts and also to the chloronium and bromonium salts, triphenyloxonium salts enter very sluggishly into phenylation reactions. Thus, triphenyloxonium chloride, bromide, iodide, and fluoborate do not, under any of the conditions tested, phenylate metallic mercury; the fluoborate does not react with copper or thallium. Phenylation of such anions as NO_2^- and N_3^- requires many hours of refluxing of the aqueous solutions. It can be accomplished to the extent of 25-27%. Compounds containing atoms with a free pair of electrons are more easily phenylated. Pyridine, for example, is phenylated at the nitrogen atom with 90% yield. Phenylation of diethylamine proceeds only in the presence of water and occurs with a yield of 60%.

EXPERIMENTAL METHODS

1. Preparation of triphenyloxonium fluoborate. To 150 g of diphenyl ether at 80-90° (bath temperature) and with vigorous stirring was added, over the course of an hour, a solution of 10.5 g of benzenediazonium fluoborate in 300 ml of acetone (which was continuously distilled during the reaction). The reaction mixture was heated another 30 minutes to complete the reaction, and after cooling it was treated 4 times with 50% aqueous acetone (10 ml). The aqueous acetone extract was extracted with ether, and, after distillation of the latter (and the acetone) under vacuum, 0.38 g (2% of theoretical calculated on the benzenediazonium fluoborate) of the water-insoluble triphenyloxonium fluoborate separated from solution. The salt was purified by reprecipitation from acetone with ether. The salt was obtained in the form of colorless crystals with a decomposition temperature of 226°, readily soluble in acetone, less soluble in alcohols, and insoluble in cold water and ether.

Found %: C 64.61, 64.46; H 4.56, 4.65. $\text{C}_{18}\text{H}_{15}\text{BF}_4\text{O}$. Calculated %: C 64.73; H 4.52.

2. Other triphenyloxonium salts - (see Table 1).

Phenylation reactions of triphenyloxonium fluoborate

Reaction with sodium nitrite in aqueous medium. A solution of 1 g of triphenyloxonium fluoborate and 2.5 g of NaNO_2 in 30 ml of water was refluxed for 25 hours, after which 0.51 g of unreacted triphenyloxonium fluoborate was recovered from the reaction mixture. The resulting nitrobenzene was not isolated, but reduction by the usual method (by the action of 1 g of metallic tin in 3 ml of concentrated hydrochloric acid) gave aniline. The latter was identified in the form of benzeneazo- β -naphthol, the yield of which was 0.09 g (25% of theoretical calculated on the triphenyloxonium fluoborate reacted); m. p. 128-129° (128.5-129.5° [3]).

Reaction with sodium azide in aqueous medium. A solution of 0.5 g of triphenyloxonium fluoborate and 2 g of NaN_3 in 30 ml of water was refluxed for 14.5 hours. The resulting phenylazide was reduced to aniline with sodium (0.5 g) in alcohol (8 ml). The latter was diazotized and coupled with β -naphthol. The yield of benzeneazo- β -naphthol was 0.1 g (27% of theoretical calculated on triphenyloxonium fluoborate); m. p. 128.5-129.5°.

TABLE 1

Anion	Obtained from:	Yield %	Decomp. temp. °C.	Analysis				
				C. %	H. %	halide %	N. %	metal %
Cl^{**}	$[(\text{C}_6\text{H}_5)_3\text{O}]^+\text{Cl}^-$ and acetone	63	193-194	67.68; 67.75; 67.60	5.90; 5.90; 6.00	11.60; 11.66; 11.09		
Br^{***}	$[(\text{C}_6\text{H}_5)_3\text{O}]^+\text{BF}_4^-$ & NaBr	72	182-182.5	65.86; 65.88; 66.09	4.78; 4.68; 4.62	24.55; 24.20; 24.42		
I	$[(\text{C}_6\text{H}_5)_3\text{O}]^+\text{BF}_4^-$ & NaI	93	177-178	57.91; 57.99; 57.78	4.03; 4.03; 4.03	34.31; 34.07; 33.92		
HgI_3^*	$[(\text{C}_6\text{H}_5)_3\text{O}]^+\text{BF}_4^-$ and NaHgI_3	92	156-157	26.15; 26.27; 26.09	1.97; 2.01; 1.82			
$(\text{C}_6\text{H}_5)_4\text{B}^+$	$[(\text{C}_6\text{H}_5)_3\text{O}]^+\text{BF}_4^-$ & $(\text{C}_6\text{H}_5)_4\text{BNa}$	100	~165	89.22; 89.33; 89.02	6.17; 6.36; 6.23			
PtCl_6^-	$[(\text{C}_6\text{H}_5)_3\text{O}]^+\text{BF}_4^-$ & H_2PtCl_6	44	184-185	47.79; 47.83; 47.92	3.17; 3.35; 3.35			21.75; 21.64; 21.63
$\text{Cr}_2\text{O}_7^{2-}$	$[(\text{C}_6\text{H}_5)_3\text{O}]^+\text{I}^-$ & $\text{K}_2\text{Cr}_2\text{O}_7$	42	~180 (darkens)	61.66; 61.56; 60.84	4.40; 4.44; 4.25			14.78; 14.62; 14.63
$\text{C}_6\text{H}_5(\text{NO}_2)_3\text{O}^+$	$[(\text{C}_6\text{H}_5)_3\text{O}]^+\text{BF}_4^-$ & $\text{C}_6\text{H}_5(\text{NO}_2)_3\text{OH}$	93	155-157	60.44; 60.36; 60.63	3.63; 3.65; 3.60		9.47; 9.19; 8.84	
ICl_4^-	$[(\text{C}_6\text{H}_5)_3\text{O}]^+\text{I}^-$ & Cl_2	94	167-171	41.95; 41.99; 41.91	2.90; 2.91; 2.93	51.32; 51.64; 55.06		

* Crystallizes with 2 molecules of water.

** Above the line - found, below the line - calculated.

*** Crystallizes with 1.5 molecules of water. Analysis presented is for the anhydrous salt.

Reaction with diethylamine in aqueous medium. A mixture of 0.25 g of triphenyloxonium fluoborate, 15 ml of diethylamine, and 6 ml of water was refluxed for 8.5 hours. The resulting diethylaniline was coupled with a p-nitrobenzenediazonium salt. The yield of 4-nitro-4'-diethylaminoazobenzene was 0.13 g (59% of theoretical calculated on triphenyloxonium fluoborate); m. p. 149-150° (151° [4]).

Reaction with pyridine. A solution of 0.2 g of triphenyloxonium fluoborate in 2 ml of pyridine was refluxed for 4 hours. After cooling, it was diluted with absolute ether. The yield of the precipitated N-phenylpyridinium fluoborate was 0.13 g (89% of theoretical). M. p. 177.5-178.5° (after recrystallization from alcohol) (178-179° [5]). The filtrate from the $[\text{C}_5\text{H}_5\text{N}^+\text{C}_6\text{H}_5]\text{BF}_4^-$ was washed several times with

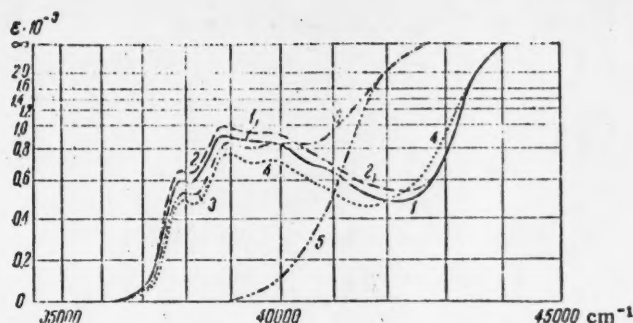


Fig. 1. Absorption spectra of triphenyloxonium salts.* 1-4) Triphenyloxonium salts: 1) chloride, 2) bromide, 3) iodide, 4) fluoborate, 5) sodium iodide; $c_M = 1 \cdot 10^{-3}$; $d = 0.5$ cm; solvent — ethanol.

* The spectra were taken in the Optical Laboratory of the Institute of Hetero-organic Compounds with a FP-1 spectrophotometer of V. I. Dianova-Klokov construction.

5% hydrochloric acid and dried over CaCl_2 . After evaporation of the ether there remained 0.05 g of diphenyl ether.

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INVESTIGATION OF THE NORMAL PARAFFINIC HYDROCARBON SYSTEMS

$C_{30} - C_{34}$ AND $C_{30} - C_{36}$

Academician A. V. Topchlev, N. A. Nechitailo,

L. M. Rozenberg, and E. M. Terentyeva

We have already remarked on the scientific and practical significance of investigations of equilibrium diagrams of systems of high-molecular-weight n-paraffinic hydrocarbons, and we have also presented the results of a study of the two binary systems eicosane - tricontane ($C_{20}H_{42} - C_{30}H_{62}$) and tricontane - dotriacontane ($C_{30}H_{62} - C_{32}H_{66}$). Eicosane and triacontane form a system of the eutectic type, while triacontane and dotriacontane form a continuous series of solid solutions.

In the present article are presented data obtained during the further study of n-paraffin systems by differential-thermal and microstructural methods.

The equilibrium diagrams of the n-paraffin binary systems triacontane - tetratriacontane ($C_{30}H_{62} - C_{34}H_{70}$) and triacontane - hexatriacontane ($C_{30}H_{62} - C_{36}H_{74}$) have not been described in the literature.

The triacontane and tetratriacontane were prepared by Kolbe electrosynthesis [2, 3], and the hexatriacontane was synthesized by the method of Wurtz. The starting materials and the final products were repeatedly recrystallized from a series of solvents, the final recrystallization being carried out with ethyl alcohol.

The degree of purity of these hydrocarbons was determined with a precision thermographic apparatus. The purity of the triacontane was 98.88 mol. %, while that of the tetratriacontane was 98.87 mol. %.

The purity of the hexatriacontane was not determined by the precision method, since we had at our disposal only a very small amount of this hydrocarbon.

As is well known, all n-paraffins with a long chain undergo reversible polymorphic transformations [4-7]. The polymorphic transition temperatures and the melting points of the hydrocarbons synthesized were determined from heating curves:

Hydrocarbon	Polymorphic transition temperature, °C	Melting point, °C
Triacontane	59.0	66.2
Tetratriacontane	68.9	73.0
Hexatriacontane	73.0	74.0

The data presented are very close to the literature values.

Recording of the thermograms was carried out with a Kurnakov photographically recording pyrometer. Sample weight was 0.05 g. The accuracy of the temperature readings was about 0.2°. The data presented in Tables 1 and 2 are average values from several parallel determinations on each mixture. Divergence in the temperature values in parallel experiments varied from ± 0.2 to $\pm 0.5^\circ$. The rate of heating (or cooling)

was 0.6–0.7°/minute. The heating curves of the mixture of the systems studied were completely identical both with respect to the number of fixed phase transitions and with respect to temperature values, in view of which only the data obtained during crystallization of the mixtures are presented.

TABLE 1

Results of Thermal Analysis of the System



Expt. No.	Wt. % $C_{30}H_{62}$	Crystallization temp., °C.		Transition temp. $\alpha - \beta$, °C.	
		initial	final	initial	final
1	98.0	72.7	71.1	68.5	67.2
2	93.1	72.5	70.9	68.3	65.7
3	90.0	72.0	68.9	66.8	63.7
4	76.6	71.6	67.6	65.3	60.1
5	70.0	71.1	67.8	65.6	60.0
6	63.0	70.2	66.2	63.7	58.9
7	50.0	69.5	65.0	62.0	57.6
8	40.0	68.8	63.6	59.7	55.5
9	29.2	67.8	63.1	59.3	55.7
10	22.0	67.5	63.5	58.9	56.0
11	14.6	66.6	62.1	57.8	55.0
12	5.0	66.4	63.1	58.0	55.1
13	2.0	66.3	64.7	58.8	56.8

TABLE 2

Results of Thermal Analysis of the System



Expt. No.	Wt. % $C_{30}H_{62}$	Crystallization temp., °C.		Transition temp. $\alpha - \beta$, °C.	
		initial	final	initial	final
1	98.0	73.0	71.9	70.2	68.4
2	95.0	71.8	71.1	70.2	66.8
3	88.3	71.7	69.4	68.6	62.4
4	80.0	70.6	67.4	66.6	57.6
5	70.0	70.0	67.2	64.8	56.6
6	60.2	69.4	66.2	62.4	56.0
7	48.0	68.3	64.2	61.0	55.2
8	36.4	67.0	63.1	58.1	54.4
9	28.0	67.0	63.0	59.2	55.0
10	20.0	65.5	62.6	57.6	54.1
11	9.6	65.8	63.5	57.7	54.4
12	2.0	66.1	64.8	57.7	56.3

The results of the thermal analysis of the binary system triacontane – tetratriacontane are presented in Table 1, and its equilibrium diagram is presented in Fig. 1.

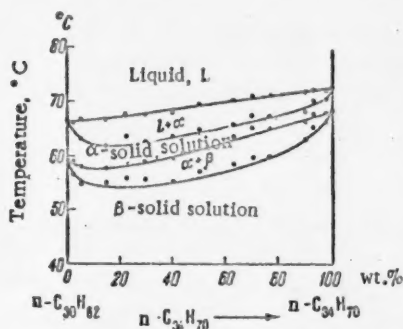


Fig. 1. Equilibrium diagram for the system $n-C_{30}H_{62} - n-C_{34}H_{70}$.

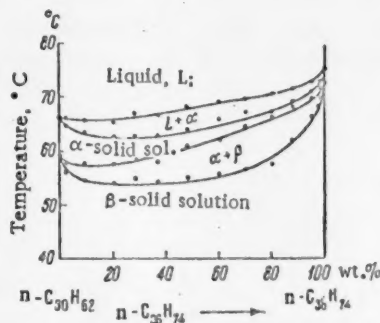


Fig. 2. Equilibrium diagram for the system $n-C_{30}H_{62} - n-C_{36}H_{74}$.

Triacontane and tetratriacontane form a system with a continuous series of solid solutions (see Fig. 1). The polymorphic modifications of the n -paraffins separating from the melt during crystallization and denoted by the letter α form a continuous solid solution, also correspondingly denoted as an α -solid solution. With a certain lowering of the temperature, the α -solid solution converts to the continuous solid solution formed by the β -modifications, which are stable at lower temperatures down to room temperature. The β -solid solution undergoes no further change with a further lowering of the temperature.

The liquidus line of the equilibrium diagram of the system $C_{30}H_{62} - C_{34}H_{70}$ is almost a straight line. This circumstance was also noted in the investigations of Piper for certain other systems of n -paraffins with long chains [8].

The linearity of the liquidus line indicates that the addition of a second component to the more highly fusible hydrocarbon causes a very small lowering of the melting point. Thus, the addition of 10% triacontane to tetratriacontane causes a lowering of the temperature of the beginning of crystallization by only 1.0°. The temperature of the end of crystallization is more markedly lowered. The temperature interval between the beginning and the end of solidification of this mixture was 3.1° at the cooling rate used.

This circumstance demonstrates that it is very difficult to judge the degree of purity of n-paraffins by melting or freezing point determinations carried out by the capillary method with a thermometer, since it is almost impossible to determine the beginning and end of crystallization, and the average temperature obtained differs very little from the melting point of the pure hydrocarbon in spite of a considerable content of the second component.

The polymorphic transition point undergoes a considerably greater lowering than the crystallization temperature with the addition of a second component. In the case considered above (10% $C_{30}H_{62}$ and 90% $C_{34}H_{70}$), it comprises 2.1° with respect to pure $C_{34}H_{70}$. The temperature interval in which the transition of the α -solid solution to the β -solid solution occurs in this mixture is 3.6°, which also shows that the transition temperature has a greater sensitivity to impurities than does the crystallization temperature.

In Table 2 are presented the results of the thermal analysis of the system triacontane - hexatriacontane. The equilibrium diagram is shown in Fig. 2.

This system is analogous to the preceding. The components form a continuous series of solid solutions over the entire concentration interval. At the higher temperatures, the solid solution formed by the α -modifications of the hydrocarbons is stable. With a lowering of the temperature, there is a transition of the α -solid solution to the β -solid solution over a rather broad temperature interval; this solid solution undergoes no change on further cooling of any of the mixtures of the system.

The liquidus line in the equilibrium diagram of this system also deviates very little from a straight line. The transition temperature is lowered considerably with an increase in the percentage content of triacontane in the mixtures. With the addition of triacontane to $C_{36}H_{74}$, the line for the beginning of the transition drops, leveling out somewhat in the left part of the diagram.

The greatest temperature interval for the transition corresponds to mixtures containing from 60 to 80% $C_{36}H_{74}$. Thus, for a mixture containing 70% hexatriacontane and 30% triacontane it is 8.2°.

Thus, the n-paraffin $C_{30}H_{62}$ - $C_{34}H_{70}$ and $C_{30}H_{62}$ - $C_{36}H_{74}$ form systems with continuous solid solutions which undergo, in the solid state, a Roozeboom Type I transition.

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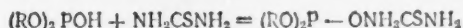
ON THE CONDENSATION OF DIALKYL PHOSPHITES WITH DERIVATIVES OF CARBOXYLIC ACIDS

V. S. Abramov

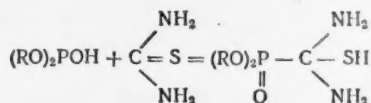
(Presented by Academician B. A. Arbuzov, June 19, 1957)

A study of the condensation of dialkyl phosphites with carbonyl compounds led us to the conclusion that aldehydes react most readily followed by ketones. As we have previously reported [2], acids, amides, and esters, even esters of formic acid in which there is an aldehyde group connected to an alkoxy group, do not react under conditions under which dialkyl phosphites condense with aldehydes and ketones [1]. This is in agreement with Watson's series of decreasing electrophilic reactivity of carbonyl groups [3]. However, research work on the reaction of dialkyl phosphites with derivatives of carboxylic acids has been continued. Experiments with derivatives of carbonic acid were crowned with success; in particular, thiourea enters into a reaction with dialkylphosphites.

Thiourea is possessed of a basic nature, and could react with dialkyl phosphites with the formation of salts:



Another possible course of reaction is the addition of dialkyl phosphites across the $>C=S$ double bond in analogy to the addition of dialkyl phosphites to a carbonyl group; the reaction can be represented as follows:



In this case, esters of diaminomercaptomethylphosphonic acids would be formed.

As our experiments showed, thiourea enters into the reaction with dialkyl phosphites on heating to a specific temperature; upon reaching this temperature, a violent reaction begins accompanied by evolution of heat from the reaction mixture; dimethyl phosphite is an example of this reaction. The reaction of dialkyl phosphites with thiourea proceeds without a catalyst, and the reaction occurs more readily and vigorously the smaller the radicals in the dialkyl phosphite: dimethyl phosphite reacts with thiourea at a temperature of 60°, while diethyl, di-n-propyl, and diisopropyl phosphites and bisethoxyethyl phosphites react on heating on the water bath, and di-n-butyl and diisobutyl phosphites react at a higher temperature. The reactions were carried out in sealed tubes.

Salts of dialkyl phosphites are derivatives of trivalent phosphorus. Addition reactions, for example, addition of sulfur are characteristic of such compounds [4]. If salts are formed by the reaction of dialkyl phosphites with thiourea, they should add sulfur and be converted to derivatives of thiophosphoric acid; if the reaction proceeds by the addition of the dialkyl phosphites across the $>C=S$ double bond with the formation of esters of diaminomercaptomethylphosphonic acid, reaction with sulfur should not occur.

As our experiments showed, the products of the reaction of diethyl phosphite and of dibutyl phosphite with thiourea do not add sulfur in benzene, aqueous alcohol, or dioxane medium. This circumstance makes possible the preliminary conclusion that, in all probability, in reactions of dialkyl phosphites with thiourea, salts are not formed, but rather the reaction proceeds by the addition of the phosphite across the $>C=S$ double bond. However, further proof of the structure of the substances obtained, a study of their properties, and establishment of the reaction mechanism are required.

The constants of the products obtained are presented in Table 1.

TABLE I

Esters of Diaminomercaptomethylphosphonic Acid

Substance obtained	M.p. °C.	P. %		Yield, %
		found	calc.	
$(CH_3O)_2P-C(NH_2)_2$ O SH	113—114	16.44; 16.20	16.66	20.5
$(C_2H_5O)_2P-C(NH_2)_2$ O SH	109—110	14.30; 14.78	14.49	49.8
$(C_4H_9O)_2P-C(NH_2)_2$ O SH	103—104	12.76; 12.84	12.81	52.0
$(C_6H_5O)_2P-C(NH_2)_2$ O SH	114—115	11.65; 11.52	11.48	30.0
iso- $(C_4H_9O)_2P-C(NH_2)_2$ O SH	144—145	11.28; 11.40	11.48	21.0

The condensation products are readily soluble in water, alcohol, and other solvents, from which they crystallize with difficulty. Recrystallization was accomplished by using dioxane as the solvent. The esters of diaminomercaptomethanephosphonic acid are greasy, paraffin-like crystals. Melting is preceded by contraction of the material into small clots, and the melting point is somewhat extended. The yield of raw products is good; however, considerable loss occurs during recrystallization.

Preliminary experiments showed that thiourea also enters into reactions with other phosphorus acids, for example, with acid esters of benzenephosphonous acid.

It was also preliminarily established that urea, formamide, and other derivatives of carboxylic acids enter into reaction with dialkyl phosphites. Work along this line continues.

We express our appreciation to A. E. Zhavoronkova for assisting in the execution of the present work.

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SYNTHESIS OF 3-HYDROXYPYRROLIDINES AND 3-HYDROXYTHIOPHANE

Yu. A. Arbuzov and Yu. A. Ovchinnikov

(Presented by Academician A. N. Nesmeyanov, July 12, 1957)

A large number of compounds containing the pyrrolidine ring are now known. However, series of compounds containing functional groups attached to the pyrrolidine ring have not been greatly studied up to the present. For example, 3-hydroxypyrrolidine, its homologs, and N-substituted 3-hydroxypyrrolidines have been studied very little. The literature [1-4] contains only reports of isolated representatives of the 3-hydroxypyrrolidines, and, as a rule, the methods of preparation differ and are specific for each compound.

In 1952, Yu. A. Arbuzov and L. I. Khmel'nitsky [5] discovered a method for the synthesis of N-substituted 3-hydroxypyrrolidines through condensation of 1,4-dibromobutanol with primary amines. However, this method is inconvenient owing to the complexity of the preparation of 1,4-dibromobutanol and the rather low yields of 3-hydroxypyrrolidines.

In 1955, W. Reppe and co-workers [6] described the preparation of 1-aryl-3-hydroxypyrrolidines by heating 1,2,4-trihydroxybutane with a mixture of a primary aromatic amine and its hydrochloride in an autoclave at 180-190°. However, the yields of 1-aryl-3-hydroxypyrrolidines were low.

It seemed of interest to find a satisfactory method for the synthesis of 3-hydroxypyrrolidine and N-substituted 3-hydroxypyrrolidines, and this work forms the basis of the present paper.

It was natural to use for this purpose 1,4-dichlorobutanol, which we obtained in high yield by the reduction of 1,4-dichlorobutanone with lithium aluminum hydride. The ketone was readily obtained in good yields by the addition of chloroacetyl chloride to ethylene in the presence of aluminum chloride [7, 8].

We found that by heating 1,4-dichlorobutanol with equimolar amounts of primary amines in absolute alcohol and in the presence of potassium carbonate, N-substituted 3-hydroxypyrrolidines are formed in high yields. This method was used by us to prepare 1-phenyl-3-hydroxypyrrolidine, 1-p-tolyl-3-hydroxypyrrolidine, 1-p-anisyl-3-hydroxypyrrolidine, 1-n-butyl-3-hydroxypyrrolidine, and 1-benzyl-3-hydroxypyrrolidine.

3-Hydroxypyrrolidine was obtained in high yield by the catalytic debenzoylation of 1-benzyl-3-hydroxypyrrolidine in the presence of palladium oxide. 3-Hydroxypyrrolidine was unknown until recently, and only in 1957 was a brief communication published by R. Kuhn [9] in which the synthesis of 3-hydroxypyrrolidine was described. It should be noted that the method of preparation of 3-hydroxypyrrolidine developed by Kuhn is considerably more complex than our method.

We prepared, in good yield, the previously unknown 3-hydroxythiophane by the condensation of 1,4-dichlorobutanol with sodium sulfide.

EXPERIMENTAL METHODS

Preparation of 1,4-Dichlorobutanol

Into a flask, fitted with a stirrer, a dropping funnel, and a reflux condenser, the upper end of which was connected to a calcium chloride tube, was placed a solution of 70.5 g (0.5 mole) of freshly prepared 1,4-dichlorobutanone in 100 ml of absolute ether. The flask was placed in an ice bath, and, while stirring, a

solution of 10 g (0.26 mole) of lithium aluminum hydride in 300 ml of absolute ether was added from the dropping funnel over a period of four hours. The reaction mixture was stirred, while cooling with ice, for an additional hour, and then 120 ml of water and 200 ml of 10% sulfuric acid were successively added dropwise to the reaction mixture. After solution of the precipitated hydroxide, the ether layer was separated, and the aqueous layer was repeatedly extracted with ether. The combined ether solutions were dried with anhydrous magnesium sulfate. The solvent was distilled, and the residue was fractionated under vacuum. 51.7 g (72%) of 1,4-dichlorobutanol with the following constants was obtained: b. p. 95-98°/18 mm; d_4^{20} 1.2922, n_D^{20} 1.4882; M_{RD} 31.90; calculated for $C_4H_8OC_2$ 31.93.

Found %: Cl 48.93. $C_4H_8OC_2$. Calculated %: Cl 49.58.

1,4-Dichlorobutanol is a thick, colorless liquid with a characteristic odor. Literature data: b. p. 95-100°/18 mm [6].

Preparation of 3-Hydroxypyrrolidines

We carried out the condensation of 1,4-dichlorobutanol with primary amines in the following manner. Into a flask, fitted with a reflux condenser, was placed the 1,4-dichlorobutanol (1 mole), the primary amine (1 mole), absolute ether, and finely ground potassium carbonate (1-1.5 mole). The flask was heated on a boiling water bath for 20-25 hours. The mixture was then cooled, and the precipitate was filtered and washed on the filter with absolute alcohol. The alcohol was distilled and the residue was fractionated under vacuum.

1-Phenyl-3-hydroxypyrrolidine. A mixture of 37 g (0.26 mole) of 1,4-dichlorobutanol, 24.2 g (0.26 mole) of aniline, 90 ml of absolute alcohol, and 54 g (0.39 mole) of potassium carbonate was heated for 20 hours. 34.7 g (82%) of 1-phenyl-3-hydroxypyrrolidine with a b. p. of 134-137°/1 mm was obtained. The substance crystallized in the form of colorless fibers during the distillation. M. p. 96-97°. Literature data: m. p. 96-97° [5]; b. p. 138-144°/1 mm [6].

1-p-Tolyl-3-hydroxypyrrolidine. A mixture of 14.3 g (0.1 mole) of 1,4-dichlorobutanol, 10.7 g (0.1 mole) of p-toluidine, 40 ml of absolute alcohol, and 15 g (0.11 mole) of potassium carbonate was heated for 25 hours. 14.5 g (82%) of 1-p-tolyl-3-hydroxypyrrolidine with a b. p. of 148-152°/1 mm was obtained. The substance crystallized in the form of colorless fibers during distillation. M. p. 85-86°. Literature data: m. p. 84-85° [5].

1-p-Anisyl-3-hydroxypyrrolidine. A mixture of 15 g (0.105 mole) of 1,4-dichlorobutanol, 13 g (0.105 mole) of p-anisidine, 50 ml of absolute alcohol, and 22 g (0.16 mole) of potassium carbonate was heated for 25 hours. 19.5 g (95%) of 1-p-anisyl-3-hydroxypyrrolidine with a b. p. of 164-166°/1 mm was obtained. The substance crystallized in the form of colorless fibers during distillation. M. p. 73-74°.

Found %: C 68.30; H 8.11; N 7.46. $C_{11}H_{15}O_2N$. Calculated %: C 68.37; H 7.82; N 7.25.

1-n-Butyl-3-hydroxypyrrolidine. A mixture of 11 g (0.077 mole) of 1,4-dichlorobutanol, 5.6 g (0.077 mole) of n-butylamine, 40 ml of absolute alcohol, and 16.2 g (0.12 mole) of potassium carbonate was heated for 20 hours. 8.9 g (81%) of 1-n-butyl-3-hydroxypyrrolidine with the following constants was obtained: b. p. 84-86°/3 mm; d_4^{20} 0.9425, n_D^{20} 1.4697; M_{RD} 42.37; calculated for $C_8H_{17}ON$ 42.41.

Found %: C 66.80; H 12.12; N 9.88. $C_8H_{17}ON$. Calculated %: C 67.08; H 11.96; N 9.98.

Literature data: b. p. 120°/22 mm; n_D^{20} 1.4659 [3].

Picrolonate of 1-n-butyl-3-hydroxypyrrolidine. A solution of 1.10 g (0.0077 mole) of 1-n-butyl-3-hydroxypyrrolidine in 30 ml of alcohol was added to a solution of 2.05 g (0.0077 mole) of picrolonic acid in 85 ml of alcohol. After 10 hours, the precipitated yellow crystals were filtered and recrystallized from alcohol. 2.95 g (95%) of 1-n-butyl-3-hydroxypyrrolidine picrolonate melting at 167-169° (with decomposition) was obtained. The crystals were bright yellow needles. Literature data: m. p. 167.5-169.5° (with decomposition) [3].

1-Benzyl-3-hydroxypyrrolidine. A mixture of 28.6 g (0.2 mole) of 1,4-dichlorobutanol, 21.4 g (0.2 mole) of benzylamine, 80 ml of absolute alcohol, and 41.4 g (0.3 mole) of potassium carbonate was heated for 25 hours. 27.3 g (79%) of 1-benzyl-3-hydroxypyrrolidine with the following constants was obtained: b. p. 138-141°/6.5 mm; d_4^{20} 1.0688, n_D^{20} 1.5528; M_{RD} 53.05; calculated for $C_{11}H_{15}ON$ 52.66.

Found %: C 74.72; H 3.77; N 7.89. $C_{11}H_{15}ON$. Calculated %: C 74.54; H 3.53; N 7.90.

The material was a thick, colorless liquid.

3,5-Dinitrobenzoate of 1-benzyl-3-hydroxypyrrolidine. A mixture of 3.31 g (0.019 mole) of 1-benzyl-3-hydroxypyrrolidine, 4.38 g (0.019 mole) of 3,5-dinitrobenzoyl chloride, and 8 ml of dry pyridine was heated on a boiling water bath for 15 minutes. Ten percent hydrochloric acid was added to the cooled mixture and the precipitate was filtered, washed with dilute hydrochloric acid, then with water, and recrystallized from methyl alcohol. 6.20 g (89%) of 1-benzyl-3-hydroxypyrrolidine 3,5-dinitrobenzoate with a m. p. of 227-228° (with decomposition) was obtained. The material was in the form of lustrous, colorless needles.

Found %: N 11.25. $C_{18}H_{17}O_6N_3$. Calculated %: N 11.32.

Catalytic debenzylation of 1-benzyl-3-hydroxypyrrolidine. 4.5 g (0.025 mole) of 1-benzyl-3-hydroxypyrrolidine was dissolved in 50 ml of absolute alcohol and hydrogenated at room temperature and ordinary pressure in the presence of 0.8 g of palladium oxide. Absorption of hydrogen was complete at the end of 8 hours, 615 ml (0°/760 mm) of hydrogen having been absorbed. The catalyst was filtered, the solvent distilled, and the residue fractionated under vacuum. 1.9 g (86%) of 3-hydroxypyrrolidine with a b. p. of 102 to 104°/12 mm was obtained.

3-Hydroxypyrrolidine is a rather thick, colorless liquid with a characteristic odor. Literature data: b. p. 102-103°/12 mm [9].

Picrolonate of 3-hydroxypyrrolidine. A solution of 0.5 g (0.0057 mole) of 3-hydroxypyrrolidine in 20 ml of alcohol was added to a solution of 1.50 g (0.0057 mole) of picronic acid in 40 ml of alcohol. After 10 hours, the yellow crystals, which had precipitated from solution, were filtered and recrystallized from alcohol. 1.80 g (90%) of 3-hydroxypyrrolidine picrolonate with a m. p. of 228-229° (with decomposition) was obtained in the form of yellow needles.

Found %: N 19.43. $C_{14}H_{17}O_6N_2$. Calculated %: N 19.88.

Literature data: m. p. 228-230° (with decomposition) [9].

Preparation of 3-Hydroxythiophane

Into a flask, fitted with a stirrer, a dropping funnel, a reflux condenser, and a thermometer, was placed a solution of 21.5 g (0.15 mole) of 1,4-dichlorobutanol in 200 ml of 50% alcohol. The solution was heated to 60°, and to it a solution of 72 g (0.3 mole) of crystalline sodium sulfide in 100 ml of water was added with stirring over a period of 40 minutes. The introduction of the sodium sulfide solution was accompanied by the evolution of heat, so that the temperature of the solution was maintained at about 60° without external heating. The mixture was heated, with stirring, on a boiling water bath for a period of 4 hours. The mixture was cooled, and 20% hydrochloric acid was added to it until the mixture had an acid reaction to litmus. The alcohol was then distilled under vacuum, and the residue was repeatedly extracted with ether. The combined ether solutions were dried with anhydrous magnesium sulfate. The ether was distilled, and the residue was fractionated under vacuum. 11.6 g (74%) of 3-hydroxythiophane with the following constants was obtained: b. p. 84-85°/7 mm; d_4^{20} 1.1762, n_D^{20} 1.5427; MR_D 27.90; calculated for C_4H_3OS 28.07.

Found %: C 46.03; H 7.68. C_4H_3OS . Calculated %: C 46.12; H 7.74.

The material was a rather thick, colorless liquid with a characteristic unpleasant odor.

3-Hydroxythiophane acetate. A mixture of 3.6 g (0.034 mole) of 3-hydroxythiophane and 7.2 g (0.092 mole) of acetyl chloride was refluxed on a water bath for a period of an hour. The excess acetyl chloride was distilled, and the residue distilled under vacuum. 3.9 g (78%) of 3-hydroxythiophane acetate with the following constants was obtained: b. p. 82-83°/7 mm; d_4^{20} 1.1502, n_D^{20} 1.5003; MR_D 37.41; calculated for $C_6H_9O_2S$ 37.43.

Found %: C 49.61; H 7.01. $C_6H_9O_2S$. Calculated %: C 49.28; H 6.89.

3,5-Dinitrobenzoate of 3-hydroxythiophane. A mixture of 2.07 g (0.02 mole) of 3-hydroxythiophane, 4.61 g (0.02 mole) of 3,5-dinitrobenzoyl chloride, and 8 ml of dry pyridine was heated on a boiling water bath

for a period of 15 minutes. The mixture was cooled, and to it was added 10% hydrochloric acid. The precipitate was filtered, washed with dilute hydrochloric acid, then with water, and recrystallized from methyl alcohol. 5.7 g (95%) of 3-hydroxythiophane 3,5-dinitrobenzoate with a m. p. of 121-121.5° was obtained in the form of lustrous plates.

Found %: N 9.65. $C_{11}H_{10}O_6N_2S$. Calculated %: N 9.39.

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A METHOD OF SYNTHESIS OF ESTERS OF ALKANEPHOSPHONOUS ACIDS

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Esters of alkanephosphonous acids are comparatively difficultly obtainable substances. Representatives of this class of compounds were synthesized in 1952 from the corresponding alkyldichlorophosphines by B. A. Arbuzov and N. I. Rizpolozhensky [1] and also by A. I. Razumov, O. A. Mukhacheva and Sim Do Khen [2, 3]. A number of diphenyl esters of phosphonous acids were prepared by G. Kamal and E. A. Gerasimova [4] by the action of diphenyl chlorophosphite on organomagnesium compounds. The esters of arylphosphonous acids, first described in the works of A. Michaelis [5] and A. E. Arbuzov [6], have been investigated with considerably more thoroughness.

The usual method for the preparation of esters of phosphonous acids is based on the reaction of the corresponding dichlorophosphines with alcoholates or with alcohols in the presence of a base. Though satisfactory methods have been developed for the synthesis of arylchlorophosphines [7, 8], preparation of alkyldichlorophosphines still presents considerable difficulties. Synthesis by means of organomercury compounds [9], which, at the present time, is the only general method, requires the use of toxic substances, and is complicated by the difficulties attending the purification of the alkyldichlorophosphines from the organomercury derivatives present. A synthesis, proposed in 1949 [10], through organolead compounds (an example was the preparation of ethyldichlorophosphine) has limited scope, since only tetraethyllead is readily available. More recently developed methods of synthesis using organocadmium [11] and organozinc [8] derivatives are free from the deficiencies indicated above but they give comparatively low yields (26-47%) of alkyldichlorophosphines.

In the present work, a general method is described for the synthesis of esters of aryl- and alkanephosphonous acids by the action of organomagnesium compounds on dialkyl chlorophosphites at a temperature of -60° .



Carrying out the reaction under low-temperature conditions makes it possible selectively to substitute alkyl or aryl radicals for the chlorine atoms of the dialkyl chlorophosphites without contamination by alkoxy groups.

A solution of the organomagnesium compound (0.11 mole of alkyl or aryl halide, 0.11 g-atom of magnesium, and 50 ml of ether) was added dropwise (15-20 minutes), with vigorous stirring, to 0.1 mole of the dialkyl chlorophosphite in 50 ml of ether with the reaction mass at a temperature of $-60 \pm 5^{\circ}$. When the addition had been completed, the ethereal solution was decanted, the residue was washed with dry petroleum ether (3 times with 50 ml portions), the solvent eliminated, and the residue distilled under vacuum. All operations were carried out in an atmosphere of dry nitrogen. The yield, constants, and analytical data for the resulting esters are presented in Table 1. Bromine compounds served as the alkyl and aryl halides; benzyl chloride and methyl iodide were exceptions. In the latter case, careful separation of the magnesium iodide was advantageous, and this was accomplished by elimination of the ether from the reaction mixture and subsequent extraction of the residue with petroleum ether.

These esters of alkanephosphonous acids readily oxidize in air and vigorously add sulfur and cuprous iodide. In order to confirm the structures of the synthesized substances, several esters of alkanethiophosphonic

TABLE 1

Exp. No.	Formula	Yield %	Boiling point, °C./press. in mm	n_D^{20}	d_4^{20}	MR		C		H		P	
						found	calc.	found	calc.	found	calc.	found	calc.
1	$\text{CH}_3\text{P}(\text{OC}_6\text{H}_5)_2$	69.5	39—40/1 mm	1.4348	0.8902	56.30	55.89	56.10 56.12	56.26	41.05 40.99	41.02	15.81 15.82	16.13
2	$\text{C}_6\text{H}_5\text{P}(\text{OC}_6\text{H}_5)_2$	64.3	59—56.5/7 mm	1.4318	0.8935	51.70	51.27	54.00 53.87	53.93	40.89 40.86	40.74	17.60 17.65	17.39
3	$\text{C}_6\text{H}_5\text{P}(\text{OC}_6\text{H}_5)_2$	70.0	47—48/1 mm	1.4370	0.8871	60.92	60.51	58.18 58.08	58.21	41.07 41.07	41.24	15.38 15.24	15.02
4	$\text{C}_6\text{H}_5\text{P}(\text{OC}_6\text{H}_5)_2$	66.4	59.8—60.3/1 mm	1.4393	0.8851	65.50	65.12	59.70 59.56	59.96	41.37 41.41	41.45	13.86 14.11	14.06
5	$\text{C}_6\text{H}_5\text{P}(\text{OC}_6\text{H}_5)_2$	68.4	68—69/1 mm	1.4420	0.8839	70.14	69.74	61.46 61.33	61.51	41.51 41.53	41.61	13.51 13.49	13.22
6	$\text{C}_6\text{H}_5\text{CH}_2\text{P}(\text{OC}_6\text{H}_5)_2$	54.5	103—104/1 mm	1.4972	0.9742	80.62	80.00	68.96 66.85	67.17	9.24 9.34	9.39	11.32 11.35	11.54
7	$\text{C}_6\text{H}_5\text{P}(\text{OC}_6\text{H}_5)_2$	63.0	97.5—98.5/1 mm	1.4993	0.9769	76.54	75.38	66.12 66.14	66.15	9.16 9.04	9.12	12.40 12.23	12.18
8	$\text{C}_6\text{H}_5\text{P}(\text{OC}_6\text{H}_5)_2$	61.5	73—74/1 mm	1.5072	1.0000	67.35	66.14	64.03 63.96	63.71	8.50 8.44	8.46	13.61 13.54	13.70
9	$\text{C}_6\text{H}_5\text{P}(\text{OC}_6\text{H}_5)_2$	53.7	62.5—63/1 mm	1.5131	1.0252	58.13	56.91	60.85 60.84	60.59	7.71 7.83	7.63	15.28 15.25	15.63
10	$\text{C}_6\text{H}_5\text{P}(\text{OC}_6\text{H}_5)_2$		81.5—83/2 mm	1.4827				64.45 64.10	64.43	9.47 9.47	9.57	12.41 12.80	12.78

Literature data: No. 2—b. p. 65–66.5°/11 mm, n_D^{20} 1.4276, d_4^{20} 0.9021 [1]. No. 3—b. p. 63–64°/3 mm, n_D^{20} 1.4353, d_4^{20} 0.8977 [1].
 No. 5—b. p. 116.5–118°/10 mm, n_D^{20} 1.4410, d_4^{20} 0.8883 [3]. No. 8—b. p. 137°/15 mm, n_D^{20} 1.4939, d_4^{20} 0.9925 [6b]. No. 9—
 b. p. 235°/237 mm, n_D^{20} 1.5120, d_4^{20} 1.0247 [12].

TABLE 2

Expt. No.	Formula	Yield %	Boiling point (m.p.) C/press. in mm	n_D^{20}	d_4^{20}	MR		C		H		P 10 Cu ₃ P ₂ O ₇		S (I)	
						found	calc.	found	calc.	found	calc.	found	calc.	found	calc.
1	CH ₃ PS (OC ₄ H ₉) ₂	87.3	69-70/1 mm	1.4622	0.9872	82.48	82.12	48.20 48.23	48.19	9.51 9.61	9.44	13.55 13.37	13.81	14.43 14.25	14.30
2	C ₆ H ₅ PS (OC ₄ H ₉) ₂	85.4	76-77/1 mm	1.4628	0.9786	67.05	66.74	50.41 50.49	50.39	9.84 9.78	9.73	13.05 13.23	13.00	13.56 13.61	13.45
3	C ₄ H ₉ PS (OC ₄ H ₉) ₂	86.6	55-56/1 mm	1.4630	1.0007	57.88	57.50	45.47 45.49	45.69	9.15 9.15	9.11	14.28 14.22	14.73	15.05 15.22	15.25
4	C ₈ H ₁₇ PS (OC ₄ H ₉) ₂	87.5	84-85/1 mm	1.4623	0.9702	71.55	71.35	52.20 52.08	52.34	10.02 10.11	9.98	12.14 12.31	12.27	12.59 12.50	12.71
5	C ₆ H ₅ P (OC ₂ H ₅) ₂ ·CuJ	71	122.5-123.5 (from) alc	—	—	—	—	30.81 30.55	30.90	3.91 3.83	3.89	38.74 38.33	38.73	38.08 33.25	32.66
6	C ₄ H ₉ P (OC ₄ H ₉) ₂ ·CuJ	74.4	129.5-130.5 (from) alc	—	—	—	—	34.47 34.58	34.58	4.65 4.73	4.60	38.37 36.39	36.12	30.77 30.69	30.46
7	C ₆ H ₅ P (OC ₄ H ₉) ₂ ·CuJ	75	88-89 (from) alc	—	—	—	—	37.77 37.55	37.81	5.39 5.23	5.21	34.21 34.01	33.83	28.90 29.19	28.53

Literature data: No. 1 - b. p. 72-74°/1 mm, n_D^{20} 1.4535, d_4^{20} 0.9848 [13]. No. 2 - b. p. 79.5-83°/2 mm, n_D^{20} 1.4533, d_4^{20} 0.9775 [13];
 b. p. 97-98°/2 mm, n_D^{20} 1.4510, d_4^{20} 0.9768 [14]. No. 3 - b. p. 69-70°/1.5 mm, n_D^{20} 1.4622, d_4^{20} 1.0005 [1]. No. 4 - b. p. 103-104°/2 mm,
 n_D^{20} 1.4580, d_4^{20} 0.9772 [14].

acids and complex compounds of the arylphosphonous esters with cuprous iodide were prepared by the usual methods (see Table 2).

In calculating the molar refractions of the phosphonous esters, a value of 7.74, proposed by A. I. Razumov and O. A. Mukhacheva [3] was used for the atomic refraction of phosphorus. In the case of the esters of alkanephosphonous acids, there was a constant excess of the found molecular refraction over the calculated amounting to 0.41; the exaltation for the arylphosphonous esters was of the order of 1.20.

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PHOTOKHLOORINATION OF ETHYLTRIKHLOOROSILANE IN THE LIQUID STATE

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There are descriptions in the literature of the chlorination of ethyltrichlorosilane by heating with sulfuryl chloride in the presence of benzoyl peroxide [1] and of photochlorination in the vapor phase with chlorine in a Kursanov apparatus [2].

We carried out the photochlorination of ethyltrichlorosilane in the liquid state with gaseous chlorine under previously described conditions [3] with irradiation by means of a 150 watt incandescent lamp. The starting material, which was free from contamination by iron compounds, had d_4^{20} 1.2393 and n_D^{20} 1.4259. Duration of the induction period was 10 minutes at a temperature of 20-30°. At the end of the induction period, gaseous chlorine was fed at a rate of 0.25-0.3 mole/hour per mole of ethyltrichlorosilane until a specified weight increase was attained. Cooling of the flask with circulating water provided for maintenance of the temperature of the liquid being chlorinated at 15-20°, at which temperature the chlorine reacted immediately; there was no coloring of the liquid.

After chlorination, the mixture was fractionated by distillation in a column with Favorsky packing equivalent to 20 theoretical plates. The compositions of the intermediate fractions were estimated from the densities.

The results of the chlorination are presented in Table 1.

The compositions of the mixtures bear witness to the unusually high yield of monochloro substituted products during photochlorination of ethyltrichlorosilane in the liquid state. With chlorination to the extent of 0.75 and of 1 mole per mole of $C_2H_5SiCl_3$, the yields of monochloro products were, respectively, 93 and 85%, based on reacted chlorosilane, while the corresponding values for diethyldichlorosilane are 78 and 12% [3], and in the case of the liquid-phase photochlorination of the closest homolog of ethyltrichlorosilane - methyltrichlorosilane - the formation of di- and trichloro products is overwhelming [4].

With degrees of chlorination of 1.5 and 2 moles of Cl_2 per mole of $C_2H_5SiCl_3$, of the three possible dichloro products, the β, β -isomer predominates in the mixtures; considerably less of the α, β -isomer is formed, and still less of the α, α -isomer (b. p. about 156°, crystalline at room temperature). Of the three possible trichloro substituted products in these mixtures, the predominant isomer boils at about 200° and is a liquid at room temperature. Calculation of the boiling points of the two liquid trichloro substituted products provides basis for the assumption that the latter is the α, β, β -isomer.

* Appreciable contamination by iron of alkylchlorosilanes leads to a sharp increase in the length of the induction period and to a decrease in the rate of the liquid-phase photochlorination reaction. Contamination with iron also causes a decrease in the yield of monochloro substitution products simultaneously with an increase in the yields of di- and polychloro substitution products.

The closeness of the boiling points of the β -chloro product and the α, α -dichloro product, on the one hand, and of the α, β - and β, β -dichloro products, on the other hand, makes it difficult to separate the highly chlorinated mixtures in a column equivalent to 20 theoretical plates. For this reason, the composition of the mixtures given in the last two columns of Table 1 are approximate, and the estimation of the ratio of di- and trichloro products has a distinctly qualitative nature.

TABLE 1

Relation of the Density, Refractive Index, Composition (in mol. %) of the Mixtures and Ratio of the Amounts of α - and β -Chloroethyltrichlorosilanes on Degree of Chlorination of Ethyltrichlorosilane

	Degree of chlorination, moles C_{12} per mole $C_2H_5SiCl_3$				
	0.75	1	1.25	1.5	2
d_4^{20}	1.3674	1.4015	1.4375	1.4752	1.5180
n_D^{20}	1.4529	1.4603	1.4671	1.4748	1.4810
$C_2H_5SiCl_3$, %	30	14	4	0	0
$CH_3ClHSiCl_2$, %	17	18.5	16		
$ClCH_2CH_2SiCl_2$, %	48	54.5	55.5	55	48
Di- and polysubstituted products and loss, %	5	13	24.5	45	82
Ratio of amounts of α - and β -isomers of $ClC_2H_4SiCl_2$	1 : 2.8	1 : 2.95	1 : 3.45	—	

Four atoms of hydrolyzable chlorine atoms were found in α, β - and β, β -dichloroethyltrichlorosilane by the action of 0.1 N aqueous sodium hydroxide, while titration in an aqueous alcohol medium with mercuric nitrate gave 3 atoms of hydrolyzable chlorine.*

In Table 2 are presented the physical constants of the chloro substituted ethyltrichlorosilanes isolated by rectification in a column equivalent to 20 theoretical plates.

TABLE 2

Substance	B. p. °C.	d_4^{20}	n_D^{20}	MR_D	
				found	calc.
$CH_3ClHSiCl_2$	137	1.3934	1.4559	38.61	38.39
$ClCH_2CH_2SiCl_2$	152	1.4100	1.4640	38.50	
$ClCH_2ClHSiCl_2$	182	1.5352	1.4853	43.41	43.23
$Cl_2CHCH_2SiCl_2$	177.2	1.5243	1.4808	43.38	
$Cl_3CCH_2SiCl_2$	~200	1.6149	1.4990	46.52	48.07

The close comparison of the results presented in the present communication with the literature data [1, 2] permits evaluation of liquid-phase photochlorination as the most efficient method for the chlorination of ethyltrichlorosilane.

* Determination of the hydrolyzable chlorine was carried out by A. M. Neshumova and L. A. Kondratyeva.

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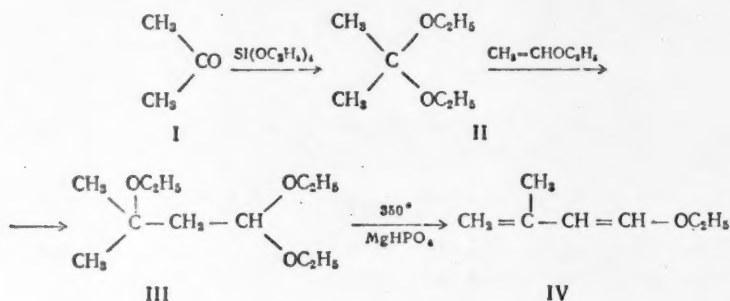
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SYNTHESIS OF ETHOXYISOPRENE

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and B. K. Krupstov

Ethoxydienes are of undoubted interest in organic chemistry. The presence in alkoxydienes of two conjugated double bonds and the reactive alkoxy group makes possible their use in the synthesis of a variety of compounds. Isoprene (1-ethoxy-3-methyl-1,3-butadiene) (IV) is of particular interest, since, owing to the presence of methyl branching at the 3-position, this compound has an isoprenoid structure, and can be used for the synthesis of important isoprenoids (citral, vitamin A, carotene, etc.).

The synthesis of ethoxyisoprene was developed and carried out for the first time by us according to the following reactions:

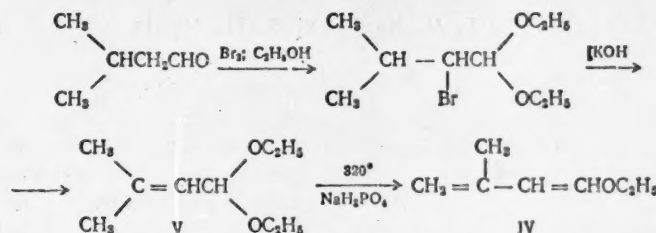


We obtained the diethyl acetal of acetone (II) by the action of tetraethoxysilane (ethyl orthosilicate) on acetone. There is available in the literature a description by Helferich [1] of the preparation of the diethyl acetal of acetone from acetone and tetraethoxysilane in a three-fold excess of ethyl alcohol and in the presence of hydrogen chloride as a catalyst. However, in numerous experiments under these conditions we obtained only trifling yields of the acetal (10-15%). We were able to obtain a high yield (92%) of this acetal by using as a catalyst 85% phosphoric acid in the presence of a small amount of ethyl alcohol (0.5 mole of alcohol per mole of tetraethoxysilane).

We then introduced the diethyl acetal of acetone into a condensation reaction with ethyl vinyl ether. It is known from the literature that acetals of aldehydes condense with ethyl vinyl ether in the presence of zinc chloride or boron trifluoride as a catalyst [2]. However, the addition of ketals to a vinyl ether is almost unstudied. The only available data are those in the patent literature on the addition of the acetals of acetone and cyclohexanone to vinyl methyl ether with low yields [3]. We were able to carry out the condensation of the diethyl acetal of acetone to ethyl vinyl ether at 0° in the presence of catalytic amounts of boron trifluoride etherate, obtaining a yield of 3-methyl-1,1,3-triethoxybutane (III) of 85% based on the acetal reacted. It was necessary to use a one-and-one half fold excess of the diethyl acetal of acetone in order to avoid further condensation of the 3-methyl-1,1,3-triethoxybutane with ethyl vinyl ether.

It has previously been shown that at 250-350° and over certain catalysts, 1,1,3-trialkoxybutane and the acetal of crotonaldehyde react to form 1-alkoxybutadiene [4, 5]. We established that on passing the vapors of 3-methyl-1,1,3-triethoxybutane (III) through a catalyst tube filled with MgHPO_4 catalyst at a temperature of 350° and a vacuum of 15-20 mm, two molecules of alcohol are split out and ethoxybutadiene (IV) is formed in 77% yield.

We also obtained ethoxyisoprene in good yield by passing the vapors of the diethyl acetal of β -methylcrotonaldehyde over NaH_2PO_4 catalyst. The diethyl acetal of β -methylcrotonaldehyde required for this reaction was prepared from isovaleraldehyde [6].



EXPERIMENTAL METHODS

Diethyl acetal of acetone (II). A mixture of 3120 g of tetraethoxysilane, 1200 ml of dry acetone, 450 ml of anhydrous ethyl alcohol, and 30 ml of 85% phosphoric acid was refluxed for 10 hours, and was then allowed to stand for a day at room temperature. The reaction mixture was treated with sodium methylate to an alkaline reaction, and distilled. The fraction boiling at 70-150° (1900 g) was agitated for 10-15 minutes with 30% sodium hydroxide (1200 ml), and was then washed with water. The material was dried with potassium carbonate and distilled. 1735 g of the diethyl acetal of acetone, b. p. 112-114° was obtained. An additional 100 g of the acetal was obtained from the wash water by extraction with ether. The total yield was 1835 g (92.5% of theoretical).

3-Methyl-1,1,3-triethoxybutane (III). To a mixture of 1300 g of the diethyl acetal of acetone and 5.2 ml of boron trifluoride etherate was added 500 g of ethyl vinyl ether while cooling with ice water and stirring vigorously. The mixture was stirred at 4-5° for an additional 3.5 hours, and was then neutralized with sodium ethylate. After two distillations, there were obtained:

- 1) 615 g of the original diethyl acetal of acetone (II) with a b. p. of 110-114°.
- 2) 903 g of 3-methyl-1,1,3-triethoxybutane (III) with a b. p. of 78°/7 mm; n_D^{20} 1.4145; d_{20}^{20} 0.8813; MR found 58.01, calculated 57.92.

Found %: C 64.55, 64.45; H 11.80, 11.77. $\text{C}_{11}\text{H}_{24}\text{O}_3$. Calculated %: C 64.66; H 11.84.

Yield based on acetal reacted, 85%.

- 3) Residue, 207 g.

Preparation of MgHPO_4 catalyst. 100 g of $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ was mixed in a porcelain cup with 190 g of water glass (sp. gr. 1.384) to the consistency of a thick paste. The resulting mass was extruded by means of a metal syringe (diameter of opening 2 mm), and the extrudate was cut into lengths of 3-4 mm. The catalyst was dried at 200° in a vacuum of 10-15 mm.

Ethoxyisoprene (1-ethoxy-3-methyl-1,3-butadiene) (IV). a) From 3-methyl-1,1,3-triethoxybutane. 600 g of 3-methyl-1,1,3-triethoxybutane (III) was passed through a ceramic catalyst tube, 60 cm long and 20 mm in diameter, filled with 100 ml of MgHPO_4 catalyst; the reaction was carried out at 350-390° and under a vacuum of 15-20 mm; the time required for the passage of the 600 g was 8 hours. The reaction product, which was collected in a trap cooled with dry ice and acetone, was washed with water, dried with

anhydrous potassium carbonate, and distilled under vacuum. There was obtained 254 g (77% yield) of ethoxyisoprene (IV) with a b. p. of 75-77°/90 mm; n_D^{20} 1.4618; d_4^{20} 0.8345; MR found 36.87, calculated 35.23.

Found %: C 75.23, 75.25; H 10.85, 10.71. $C_7H_{12}O$. Calculated %: C 75.00; H 10.71.

b) From the diethyl acetal of β -methylcrotonaldehyde (V). 30 g of the diethyl acetal of β -methylcrotonaldehyde was passed through the above-described catalyst tube filled with 60 g of NaH_2PO_4 catalyst [5]; the reaction was carried out at a temperature of 320° and a vacuum of 25 mm, and 50 minutes were required for the passage of the 30 g; the condensate was collected in a trap cooled with dry ice and acetone. After the usual treatment and vacuum distillation, 11.6 g (54%) of ethoxyisoprene (IV), b. p. 75-77°/20 mm, was obtained.

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**ISOTOPE-EXCHANGE REACTION OF SYMMETRICAL ORGANOMERCURY
COMPOUNDS OF THE AROMATIC SERIES WITH
METALLIC MERCURY TAGGED WITH Hg²⁰³**

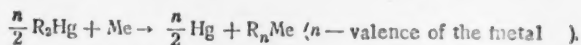
O. A. Reutov and G. M. Ostapchuk

(Presented by Academician A. N. Nesmeyanov, October 25, 1957)

In connection with an investigation of the mechanism of substitution at a carbon atom using organomercury compounds [1-4], we undertook a systematic study of the reactivity of various types of organomercury compounds in isotope-exchange reactions with metallic mercury and mercury halide [5].

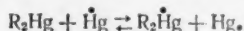
In the present communication are reported some results of a study of isotope exchange between diarylmercury and metallic mercury tagged with the radioactive isotope Hg²⁰³.

A well-known method of synthesizing organometal compounds is by the interaction of organomercury compounds with metals (Li, Na, Be, Mg, Zn, Cd, Al, In, Sn, Sb, and Bi).

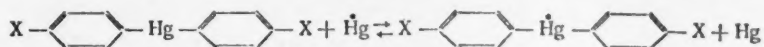


The reaction proceeds at room temperature with the more reactive metals, but in the case of heavy metals, heating to 120-130° is required. The mechanism of the reaction has not been studied.

The simplest conceivable type of this reaction is that of isotope exchange:



We found that, unexpectedly, symmetrical organomercury compounds of the aromatic series react with mercury under very mild conditions. The rate of the isotope exchange reaction



depends essentially on the nature of X.

The reactions were carried out in organic solvents with vigorous stirring at a standard rate (1500 ± 200 rpm) in a thermostatted system.

For the determination of the percent exchange, the diarylmercury was separated from the reaction mixture as follows: water was added to the dioxane or pyridine solution after filtering from the mercury; the precipitated diarylmercury was recrystallized from an appropriate solvent until a constant melting point and a constant radioactivity were attained. If benzene or xylene was used as the solvent, the diarylmercury was precipitated with petroleum ether. For the radioactivity measurements, the preparations were deposited (by

feeding the solutions dropwise) on a 20 mm diameter filter, lacquered with organic glass (1 g of plexiglass per 100 ml of dichloroethane), and dried.

The radioactivity of the diarylmercury was measured using a B-2 apparatus with the aid of MST-17 end window counters and MS-4 γ -counters.

The following figures give an idea of the rate of isotope exchange in the reaction under consideration.

For diphenylmercury. In xylene at 140° (concentration of diphenylmercury, 0.43 mole/liter; of mercury, 3.4 mole/liter), equilibrium was established after 30 minutes.

In dioxane at 60° (concentration of diphenylmercury, 0.11 mole/liter; of mercury, 1.7 mole/liter), equilibrium was established after 2 hours and 45 minutes.

For bi-p-anisylmercury. In dioxane at 60° (concentration of bi-anisylmercury, 0.088 mole/liter; of mercury, 1.74 mole/liter), equilibrium was reached after 1 hour.

In benzene at 20° (concentration of bi-anisylmercury, 0.05 mole/liter; of mercury, 0.87 mole/liter), equilibrium was established after 16 hours.

Exchange was accelerated by an increase in temperature and, to a certain extent, by an increase in the excess of metallic mercury. No effect of the nature of the solvent on the reaction rate was noted.

TABLE 1

Results of Isotope Exchange Between Organomercury Compounds and Mercury in Pyridine

Formula of the Organomercury Compound	Expt. No.	Percent exchange at various times														
		0.25 hrs.	0.5 hrs.	0.75 hrs.	1 hr.	1.5 hrs.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	6.5 hrs.	7 hrs.	7.5 hrs.	8 hrs.	9 hrs.
$(\text{CH}_3\text{O}-\text{C}_6\text{H}_4)_2\text{Hg}$	1	9	14	26	46	78	86	86	—	—	—	88	—	—	—	—
	2	11	25	41	54	75	89	100	—	—	—	—	—	—	—	—
$(\text{CH}_3-\text{C}_6\text{H}_4)_2\text{Hg}$	1	—	—	—	21	37	51	—	79	—	83	—	—	—	—	—
	2	—	—	—	18	37	62	82	88	—	92	—	—	—	—	—
$(\text{C}_6\text{H}_5)_2\text{Hg}$	1	—	—	—	3	—	—	22	—	—	80	—	—	—	100	—
	2	—	—	—	3	—	—	—	—	—	82	—	—	—	—	—
	3	—	—	—	3	—	11	26	58	—	83	—	82	—	—	—
$(\text{Cl}-\text{C}_6\text{H}_4)_2\text{Hg}$	1	—	—	—	—	7	—	16	—	28	—	—	—	—	48	—
	2	—	—	—	—	7	—	19	—	40	—	—	—	—	58	—
	3	—	—	—	—	11	—	28	—	48	—	—	—	—	62	—
$(\text{O}_2\text{N}-\text{C}_6\text{H}_4)_2\text{Hg}$	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	0	—	4	—	11	—	—	—	—	—	—	—

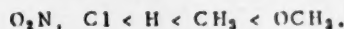
Notes. 1) The reactions were carried out in pyridine at 60°, the concentration of the organomercury compound was 0.028 mole/liter; mercury was used in 50-fold gram-equivalent excess. An exception was Experiment No. 1, where the concentration of the organomercury compound was 0.026 mole/liter, and mercury was taken in 100-fold excess.

2) In all cases, the percent exchange is given as percent of equilibrium.

Further, we decided to study the dependence of the rate of isotope exchange on the nature of the substituent X. For this purpose, we carried out a series of experiments in pyridine under identical conditions.*

* All experiments were carried out in the same 250 ml flask, fitted with a Witt stirrer, at 1500 ± 200 rpm.

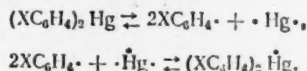
The results of these experiments are presented in Table 1; from these data, it follows that the effect of the nature of the substituent X on the rate of this isotope exchange reaction is given by the following series of increasing rate:



The accuracy of our experiments* did not permit establishing which of the organomercury compounds — dinitrophenylmercury or dichlorophenylmercury — reacts more rapidly with metallic mercury.

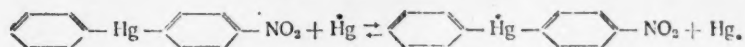
That isotope exchange proceeds under very mild conditions, especially in the case of bisphenylmercury, rapidly reacting with metallic mercury even in the cold** merits attention.

Under such mild conditions, it is hardly possible for the reaction to proceed through decomposition of the diarylmercury and the formation of free radicals:



Apparently, the reaction proceeds directly between molecules of diarylmercury and metallic mercury.

The results of isotope exchange with phenyl-p-nitrophenylmercury are in support of this:



After reaching isotope equilibrium, only the original phenyl-p-nitrophenylmercury is found in the reaction mixture. If the reaction proceeded through the formation of phenyl and nitrophenyl free radicals, $(C_6H_5)_2Hg$ and $(O_2NC_6H_4)_2Hg$, along with $C_6H_5\text{—Hg—C}_6H_4\text{NO}_2$, would have to be present in the reaction mixture after establishment of isotope equilibrium.

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* In Table 1, for each organomercury compound are presented the results of two or three parallel experiments. A comparison of the original data shows that, in the majority of cases, reproducibility averaged approximately 10%.

** As we have shown, in contrast with organomercury compounds, isotope-exchange reactions of organoantimony compounds proceed with an appreciable rate only at temperatures above 160°.



*** Original Russian pagination. See C. B. Translation.

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* See C. B. Translation.

** In Russian.

ON THE FEASIBILITY OF THE CATALYTIC DEHYDROGENATION OF SILICOHYDROCARBONS

B. N. Dolgov, G. V. Golodnikov, and K. G. Golodova

(Presented by Academician A. V. Topchlev, August 5, 1957)

The literature contains no indications as to the feasibility of catalytically dehydrogenating silicoparaffins. B. N. Dolgov, G. V. Golodnikov, and N. E. Glushkova, studying the transformations of tetraethylsilane over a chromium catalyst, found that, under the conditions used, catalytic dehydrogenation of tetraethylsilane does not occur [1]. Continuing work in this direction, we have succeeded in selecting a catalyst* and determining conditions for the dehydrogenation of one of the mixed tetraalkylsilanes — trimethylbutylsilane.

Experiments carried out at the same space rate (30) showed that yields of trimethylbutenylsilane of 6.2-8.6% calculated on the trimethylbutylsilane used are obtained at temperatures of 550-575° (Table 1).

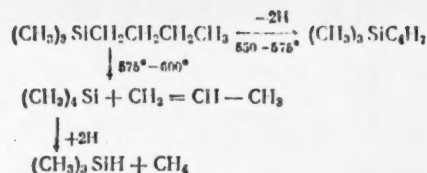
TABLE 1

Temp. °C.	Yield of condensate, % of silicohydrocarbon used	Thiocyanate number of condensates	Content of trimethylbutenylsilane in condensates, %	Yield, % of silicohydrocarbon used		
				trimethylbutenylsilane	hydrogen	propylene
475	77.6	9.7	4.9	3.6	1.8	2.0
500	84.0	7.3	3.7	3.1	1.1	1.7
525	78.7	7.8	3.9	3.1	1.3	4.2
550	69.4	17.7	9.0	6.2	1.6	3.6
575	41.3	41.4	20.8	8.6	6.2	16.3
600	22.0	49.8	25.4	5.6	7.2	18.0

The catalyst is distinguished by high stability; during a continuous, 20-hour run, the yield of silico-olefin remained constant, and silicon deposits were not found on the catalyst. The indicated yields of trimethylbutenylsilane can be considerably increased by repeated passage of the condensates over the catalyst, since the condensates contain a considerable amount of unchanged trimethylbutylsilane.

Along with the dehydrogenation reaction, some side reactions connected with the thermal decomposition of trimethylbutylsilane occurred, particularly at higher temperatures (575-600°). Of particular interest was the formation of tetramethylsilane and propylene, which proceeds with the rupture of a C-C bond in the butyl radical. There is observed, at these temperatures, destructive dehydrogenation of the resulting tetramethylsilane by hydrogen formed during the dehydrogenation of the trimethylbutylsilane. These transformations can be represented as follows:

* The authors express their appreciation to Yu. A. Gorin and S. M. Monoszon who kindly made available to them the above-mentioned catalyst.



The content of silicoolefin in the condensates was calculated from the thiocyanate numbers, which were determined by the method of A. A. Bugorkova, L. N. Petrova, and V. M. Rodionov [2]. The thiocyanation was carried out after a 5-minute refluxing of the condensate for removal of $(\text{CH}_3)_3\text{SiH}$ — a side-reaction product.

The following isomers of trimethylbutenylsilane are theoretically possible: $(\text{CH}_3)_3\text{SiCH} = \text{CHCH}_2\text{CH}_3$ (cis- and trans-forms) (I), $(\text{CH}_3)_3\text{SiCH}_2\text{CH} = \text{CHCH}_3$ (cis- and trans-forms) (II), and $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH} = \text{CH}_2$ (III). However, only trimethyl- γ -butenylsilane (III) is known. We were unable to isolate the silicoolefin in a pure form, since all of the isomers of trimethylbutenylsilane must have boiling points which are close together and which are close to that of the original trimethylbutylsilane. Fractions boiling at 109–111°, 111–114°, and 115–116° were obtained by repeated distillation of the condensates. The constants of the 109 to 111° fraction, which was the richest in silicoolefin, are compared in Table 2 with the properties of the known γ -isomer (III) and the original trimethylbutylsilane.

TABLE 2

Silicohydrocarbon		B. p. °C.	d_4^{20}	n_D^{20}
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH} = \text{CH}_2$	(3)	111.5–112 (750 mm)	0.7358	1.4148
Fraction, 109–111°		109–111	0.7375	1.4117
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	(4)	115	0.7181	1.4030

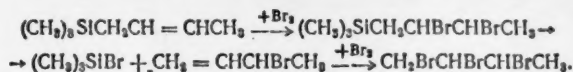
The silicoolefin obtained by us is apparently trimethyl- α -butenylsilane (I). Thus, in the Raman spectra of the combined 109–111° and 111–114° fractions, along with frequencies characteristic of trimethylbutylsilane, were observed frequencies in the region of multiple bonds: 1588, 1607, and 1628 cm^{-1} . That there is an increase in the double-bond frequency from 1594 cm^{-1} in vinylsilanes to 1623 cm^{-1} in isocrotylsilanes is known from the work of A. D. Petrov and co-workers [5]. Consequently, a transfer of the double bond from the second position to the end of the chain causes an increase in its characteristic frequency of 30 cm^{-1} , a shift which is ordinarily observed in alkenes. Further, it is known that in isocrotylsilanes there is an association of stable frequencies: 1064, 1310, 1370, and 1623 cm^{-1} . Lines at 1056, 1309, 1373, and 1628 cm^{-1} were present in our spectrum. The formation of trimethyl- β -butenylsilane (II) and trimethyl- γ -butenylsilane (III) is refuted by the absence in the spectrum of frequencies characteristic of β and γ -alkenylsilanes (1640–1655 cm^{-1}) and of a line at 3080 cm^{-1} , which is characteristic of compounds with a $=\text{CH}_2$ group at the end of the chain. Thus, optical analysis indicates the presence in the reaction products of trimethyl- α -butenylsilane, possibly as a mixture of the cis- and trans-isomers.

The absence of the β -isomer (II) was also confirmed by an investigation of the rate of thiocyanation of the silicoolefin obtained. It is known that with β -alkenylsilanes the addition of thiocyanogen is almost complete after 5 minutes, while α - and γ -alkenylsilanes are completely reacted with thiocyanogen only after a day [5]. In our case, addition of thiocyanogen occurred to the extent of only 5% in 5 minutes, 7.5% in an hour, but was complete in a day's time.

Finally, that a stable dibromide of the trimethylbutenylsilane was obtained also indicates the absence of the β -isomer. The dibromide was prepared from the condensates from experiments at 575° by the slow addition of an 0.5 N solution of bromine in chloroform while stirring and cooling externally with ice. The dibromide had a b. p. of 88-90°/8 mm, d_4^{20} 1.3581 and n_D^{20} 1.4918.

Found %: Br 55.68, 55.79. $C_7H_{16}Br_2Si$. Calculated %: Br 55.52.

It can be assumed that had the β -isomer been present in the bromination products, there would also have been present $(CH_3)_3SiBr$ - the β -decomposition product:



Tetramethylsilane was obtained in a pure form during the distillation of the condensates as a fraction boiling at 26-27°, d_4^{20} 0.6428 and n_D^{20} 1.3601 (according to [6], b. p. 26.5°, d_4^{20} 0.646, n_D^{20} 1.3591).

Propylene which was present in the gaseous products of the experiments was isolated as the dibromide with a b. p. of 141-142°, d_4^{20} 1.9322 and n_D^{20} 1.5200 (according to [7], b. p. 141.6°, d_4^{20} 1.933, n_D^{20} 1.5203).

Found %: Br 78.84, 78.94. $C_3H_6Br_2$. Calculated %: Br 79.17.

Trimethylsilane (b. p. 9°), found in the gaseous products of the experiments), was converted during the bromination to $(CH_3)_3SiBr$, as indicated by the presence of a fraction boiling at 82-84° obtained during the distillation of the bromination products. After treatment of this fraction in ether solution with 1 N NaOH and subsequent purification, a fraction boiling at 98-99° (n_D^{20} 1.3860) was obtained, which was $(CH_3)_3SiOH$ (according to [8], b. p. 100°, n_D^{20} 1.3880).

Methane was determined by combustion at 900° in a VTI gas analysis system.

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** In Russian.

SYNTHESIS OF SOME CARBON-CARBON CARBOHYDRATE DERIVATIVES

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(Presented by Academician A. I. Oparin, July 23, 1957)

As reported previously, the organomagnesium method gives good results in the synthesis of carbon-carbon derivatives of D-glucose, D-galactose, D-xylose, and L-arabinose containing various aglucones [1-4].

In the present work, this method was used to prepare some new compounds: phenyltetraacetylglactose, o-tolyltriacylxylose, allyltetraacetylglactose, and allyltriacylarabinose. It was established that acetylated allyl sugars can add a molecule of chlorine, bromine, or thiocyanogen across the double bond of the allyl radical. Halo derivatives of the previously synthesized phenyltriacylxylose were also prepared. Aceto-chloromonoses, which were the starting materials in the syntheses of the carbon-carbon derivatives of carbohydrates, were prepared by treatment of the sugar acetates with phosphorus pentachloride and aluminum chloride in chloroform solution.

EXPERIMENTAL

The glucose and galactose β -pentaacetates and the xylose β -tetraacetate, all of which were required in the work, were prepared by acetylation of the monosaccharides with acetic anhydride in the presence of anhydrous sodium acetate [5-7].

The α -chlorotetraacetylglucose was prepared by the method of Hudson and Johnson [8].

Using this same method, α -chlorotetraacetylglactose (yield 79% of theoretical) and α -chlorotriacylxylose (yield 41% of theoretical) were prepared by refluxing the sugar acetates with phosphorus pentachloride and aluminum chloride in chloroform solution.

The β -chlorotriacetyl-L-arabinose was prepared from L-arabinose by a new method in a single stage without isolating the crystalline tetraacetate.

Preparation of β -chlorotriacetyl-L-arabinose. 25 g (0.166 mole) of L-arabinose was mixed with 20 g of anhydrous sodium acetate, 120 ml of acetic anhydride was added, and the mixture was heated on a water bath (90-100°) with efficient refluxing.

After heating for 2 hours, the mixture was poured, with stirring, into 500 ml of ice water. After 2 hours, the tetraacetate was extracted with 120 ml of chloroform, the extract was washed with water and with a solution of sodium bicarbonate, and dried over calcium chloride. The dried chloroform solution was refluxed for 2 hours with 20.9 g (0.1 mole) of phosphorus pentachloride and 10 g (0.074 mole) of aluminum chloride. The solution was poured into ice water, the chloroform layer was separated, washed with a solution of sodium bicarbonate and then with water, dried with calcium chloride, and decolorized with activated carbon. The clear solution was diluted two-fold with petroleum ether, and evaporated to dryness. After removal of the solvent, β -chlorotriacetyl-L-arabinose separated in the form of colorless crystals, m. p. 146-147°. The yield was 18 g (37% of theoretical).

Phenyltetraacetylgalactose. Phenyltetraacetylgalactose was prepared from 3.93 g (0.16 mole) of magnesium, 25.2 g (0.16 mole) of bromobenzene, and 5 g (0.0136 mole) of acetochlorogalactose by the method previously proposed for the synthesis of antisyltetraacetylglucose [1].

After the usual treatment, the phenyltetraacetylgalactose was isolated in the form of a thick, transparent sirup which could not be crystallized. The material was soluble in the usual organic solvents and insoluble in water. The yield was 2.7 g (43% of theoretical). 0.22 g of benzoic acid was obtained by oxidation of 1.2 g of the sirup.

The material is described here for the first time.

Found %: C 58.45; H 5.70. $C_{26}H_{24}O_9$. Calculated %: C 58.82; H 5.88.

o-Tolyltetraacetylxylose. The substance was prepared from 3.93 g (0.16 mole) of magnesium, 27.5 g (0.16 mole) of o-bromotoluene, and 5 g (0.0186 mole) of acetochloroxylose. The o-tolyltetraacetylxylose was isolated by the usual method, and was purified by recrystallization from butanol. The product was obtained in the form of colorless crystals in a yield of 2.8 g (47% of theoretical). M. p. 110-111°. The substance is soluble in alcohol, ether, benzene, and acetone and insoluble in water. Phthalic acid was obtained on oxidation of this substance.

The substance is described here for the first time.

Found %: C 61.84; H 6.30. $C_{18}H_{22}O_7$. Calculated %: C 61.71; H 6.28.

Dibromophenyltriacylxylose. To a solution of 0.5 g (0.0013 mole) of previously prepared phenyltriacylxylose [2] in 10 ml of glacial acetic acid was added 1.8 g (0.011 mole) of bromine. After an hour, the mixture was poured into water. The dibromophenyltriacylxylose was isolated in the usual manner as a colorless sirup which crystallized on standing. After recrystallization from isopropyl alcohol, colorless crystals with a m. p. of 80-81.5° were obtained. The yield was 0.58 g (82% of theoretical).

Oxidation of the substance with an alkaline potassium permanganate solution gave 3,5-dibromo-4-ethoxybenzoic acid.

The substance is described here for the first time.

Found %: Br 29.44. $C_{19}H_{21}O_8Br_2$. Calculated %: Br 29.79.

Dichlorophenyltriacylxylose. Dichlorophenyltriacylxylose was obtained in the form of a colorless, uncrystallizable sirup by chlorination of 0.5 g (0.0013 mole) of phenyltriacylxylose with a solution of 0.8 g (0.012 mole) of chlorine in 10 ml of carbon tetrachloride. The yield was 0.45 g (76% of theoretical).

The substance is described here for the first time.

Found %: Cl 15.61. $C_{19}H_{21}O_8Cl_2$. Calculated %: Cl 16.0.

Dibromoallyltriacylxylose. 0.5 g (0.0016 mole) of the previously described allyltriacylxylose [3] was dissolved in 10 ml of acetic acid, and 1.8 g (0.011 mole) of bromine was added to the solution. After standing for one hour, the solution was poured into ice water, extracted with ether, the ether extract was washed with a weak solution of alkali and then with water, and dried over calcium chloride. The residue obtained by distillation of the ether was dissolved in a small amount of hot butanol, and on cooling, the butanol solution, dibromoallyltriacylxylose separated in the form of colorless needles with a m. p. of 123-124°.

The substance is described here for the first time.

Found %: Br 34.85. $C_{14}H_{20}O_7Br_2$. Calculated %: Br 34.79.

Dibromoallyltetraacetylglucose. Bromination of 0.5 g (0.0014 mole) of allyltetraacetylglucose with a solution of bromine in glacial acetic acid under the conditions given above led to the formation of dibromoallyltetraacetylglucose. White crystals with a m. p. of 63.5-65° were obtained by recrystallization from isopropyl alcohol. The yield was 0.57 g (80% of theoretical).

The substance is described here for the first time.

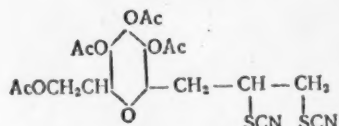
Found %: Br 29.89. $C_{11}H_{24}O_9Br_2$. Calculated %: Br 30.07.

Dithiocyanatoallyltetraacetylglucose. To a solution of thiocyanogen, prepared from 0.3 g (0.019 mole) of ammonium thiocyanate and 0.31 g of bromine in 5 ml of acetic acid, was added a solution of 0.7 g (0.0018 mole) of allyltetraacetylglucose [1] in 12 ml of acetic acid.

After standing in the sunlight for an hour, the mixture was poured into water, the water solution twice extracted with ether, the ether extract was washed with water and then with soda solution, and, after decolorizing with activated carbon, the ether solution was dried with calcium chloride. Distillation of the ether gave a colorless sirup which we were able to crystallize from isopropyl alcohol. The substance was obtained in the form of colorless crystals with a m. p. of 112-113°. The yield was 0.73 g (72% of theoretical). The substance was soluble in alcohol, ether, benzene, and acetone and insoluble in water and petroleum ether.

Found %: N 5.51; S 13.26. $C_{16}H_{24}O_9N_2S_2$. Calculated %: N 5.73; S 13.11.

Obviously, the structure of the substance must be represented by the following formula:



The substance is described here for the first time.

Dithiocyanatoallyltriacetylxylose. Dithiocyanatoallyltriacetylxylose was obtained by the above-described method from 1 g (0.0032 mole) of allyltriacetylxylose and a solution of dithiocyanogen in acetic acid; the material was obtained in the form of pale yellow needles which, after recrystallization from aqueous ethyl alcohol, melted at 85.5-88°. The yield was 1.23 g (88% of theoretical).

The substance is described here for the first time.

Found %: N 6.52; S 15.50. $C_{16}H_{20}O_7N_2S_2$. Calculated %: N 6.72; S 15.37.

The following substances were obtained in the form of uncrystallizable sirups: allyltriacetylglucose (yield 43% of theoretical), dibromoallyltriacetylglucose, dichloroallyltriacetylglucose, dithiocyanatoallyltriacetylglucose, allyltetraacetylglucose, (yield 24% of theoretical), dibromoallyltetraacetylglucose, and dichloroallyltetraacetylglucose.

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DOUBLE SALTS OF LANTHANUM, CERIUM, PRASEODYMIUM, AND NEODYMIUM WITH TRIPHENYLBENZYLARSONIUM NITRATE

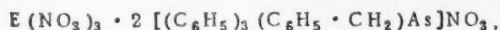
G. V. Medoks

(Presented by Academician I. I. Chernyaev, October 3, 1957)

As was previously shown, tetraphenylphosphonium nitrate [1] and chloride [2] can form double salts with the nitrates or chlorides, respectively, of lanthanum, cerium, neodymium, and praseodymium. These salts are readily crystallizable from ethanol and a number of other organic solvents. They are decomposed by water into the individual components. Partial dissociation of the complex ions proceeds during solution of these compounds in organic solvents, and the dissociation is increased by the addition of chloroform, which forms with the tetraphenylphosphonium salts crystal solvates which are readily soluble in chloroform. This explains why there is an increase in the solubility of these salts in ethanol after the addition of chloroform in spite of the insolubility of these salts in the latter.

The differences in the dissociation constants of complex ions of this type, the unequal tendency to undergo hydrolysis or cleavage with the participation of chloroform — all these factors, in total, lead to the appearance of a substantial variance in the solubilities of the double salts formed by the rare earth elements with salts of organic bases, even in the case of those elements which are very close together, for example, praseodymium and neodymium. These considerations lend a special significance to the further study of similar compounds.

As we showed, triphenylbenzylarsonium nitrate is comparatively readily available, and at the same time it can, by interaction with nitrates of the rare earth elements of the cerium group, form double salts which readily crystallize from ethanol in the form of plates, possess different melting points, and which are decomposed into their components by the action of water. These nitrates separated from 96% ethyl alcohol without water or alcohol of crystallization, and have compositions corresponding to the formula



where E is a La, Ce, Pr, or Nd atom.

The solubility of these double salts in this solvent decreased from the lanthanum to the neodymium salt, i.e., with an increase in the stability of the complex ion $[E(NO_3)_5]^{-2}$. At the same time, the solubility was greater than that of the corresponding tetraphenylphosphonium double salt.

Double salt from lanthanum and triphenylbenzylarsonium nitrates, $La(NO_3)_3 \cdot 2[(C_6H_5)_3(C_6H_5CH_2)As]NO_3$. Triphenylarsine was prepared by the method of Michaelis [3] as modified by Pope and Turner [4]. Triphenylbenzylarsonium bromide was prepared by heating the triphenylarsine with benzyl bromide, and the nitrate was prepared from the bromide. The lanthanum nitrate contained small amounts of neodymium and praseodymium as impurities.

0.68 g of $La(NO_3)_3 \cdot 6H_2O$ was dissolved in 2 ml of 96% ethanol, and 1.44 g of triphenylbenzylarsonium nitrate was introduced into the solution. The mixture was then heated on a water bath until solution of the substance was complete. Large, thin, transparent, colorless plates separated from the solution on standing in

a vacuum desiccator over sulfuric acid. After suction-filtering the mother liquor, washing with alcohol, drying, etc., there was obtained 1.49 g of product with a m. p. of 158.2-159.5°. An additional 0.14 g of the double salt was obtained from the mother liquor. The total yield of raw salt was 84.2% of theoretical. Recrystallization from 0.7 ml of ethanol gave 1.18 g of the pure material with a m. p. of 159.5 g.

Found %: La 11.30, 11.33. $\text{La}(\text{NO}_3)_3 \cdot 2[(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{As}]\text{NO}_3$. Calculated %: La 11.26.

Lanthanum oxide prepared from this salt was almost colorless.

The lanthanum double salt was very readily soluble in 96% ethanol, especially when hot. It was practically insoluble in chloroform, ethyl ether, and hydrocarbons. It was readily soluble in a mixture of 96% ethanol and chloroform.

Trivalent cerium and triphenylbenzylarsonium double nitrate, $\text{Ce}(\text{NO}_3)_3 \cdot 2[(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{As}]\text{NO}_3$.

"Pure" cerium nitrate $[\text{Ce}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$ served as the starting material. It contained "didymium" salt as an impurity.

A solution of 1.09 g of this nitrate in 5 ml of 96% ethanol was mixed with a solution of 2.3 g of triphenylbenzylarsonium nitrate in the same amount of alcohol, and the mixture was concentrated by evaporation to a total weight of 9 g. Crystallization from the slightly yellowish solution did not begin at once on cooling. It was completed during standing of the solution containing precipitated crystals in a desiccator over sulfuric acid. After suction filtering, washing of the crystals with alcohol, etc., 2.41 g of the double salt with a m. p. of 161.75-162.25° was isolated, and on condensation of the mother liquor an additional 0.21 g of the same substance with a m. p. of 162°, with decomposition, was obtained. The total yield of raw cerium salt was 86.1% of theoretical. 2.2 g of the pure salt with a m. p. of 163.75-164° was obtained by recrystallization from 1.6 ml of hot ethanol.

Found %: Ce 11.24; N 5.59. $\text{Ce}(\text{NO}_3)_3 \cdot 2[(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{As}]\text{NO}_3$. Calculated %: Ce 11.26; N 5.63.

The double nitrate of trivalent cerium with triphenylbenzylarsonium nitrate crystallized from 96% ethanol in the form of slightly yellowish plates; it was less soluble in this solvent than the analogous lanthanum salt. It was practically insoluble in ethyl ether, chloroform, and hydrocarbons. It was appreciably soluble in boiling isoamyl alcohol. Decomposition set in when the salt was heated above its melting point.

Praseodymium and triphenylbenzylarsonium double nitrate, $\text{Pr}(\text{NO}_3)_3 \cdot 2[(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{As}]\text{NO}_3$.

0.69 g of hydrated praseodymium nitrate, containing neodymium nitrate as an impurity, was dissolved in 3.5 ml of hot 96% ethanol and mixed with a hot solution of 1.67 g of triphenylbenzylarsonium nitrate in 3 ml of this same alcohol. At this, the green color of the praseodymium salt changed to yellow. Then followed condensation of the solution by evaporation on a water bath and crystallization by cooling. The coarse lemon-yellow crystals were filtered under reduced pressure, and washed with alcohol. After drying, the yield of salt was 1.84 g, m. p. 164.25-164.5°. An additional 0.15 g of the double nitrate was isolated from the mother liquor. The remaining solution was noticeably rose colored. The total yield of raw product was 83.5% of theoretical. Recrystallization from 3.3 ml of boiling alcohol gave 1.56 g of the pure compound with a m. p. of 165-165.25°.

Found %: N 5.57. $\text{Pr}(\text{NO}_3)_3 \cdot 2[(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{As}]\text{NO}_3$. Calculated %: N 5.62.

Praseodymium and triphenylbenzylarsonium double nitrate crystallized from ethanol in the form of yellowish green tablets, and was less soluble in alcohol than the analogous cerium salt. It was practically insoluble in ethyl ether, chloroform, and hydrocarbons.

Neodymium and triphenylbenzylarsonium double nitrate, $\text{Nd}(\text{NO}_3)_3 \cdot 2[(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{As}]\text{NO}_3$.

To a solution of 1.23 g of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 6 ml of 96% ethanol was added a solution of 2.78 g of triphenylbenzylarsonium nitrate in 5 ml of the same solvent, the latter solution having been prepared by heating. The crystals, which precipitated after removal of 7.8 g of alcohol by evaporation on a water bath and after cooling, were filtered, washed with alcohol, and dried. The yield was 3.11 g. 0.13 g of the original triphenylbenzylarsonium nitrate and only 0.04 g of the double salt could be recovered from the mother liquor. The total yield of double salt was 89.9% of theoretical. 2.88 g of product with a m. p. of 165.75-166° was obtained by recrystallization from hot ethanol. The pure product, obtained after a second recrystallization melted at 166.25°.

Found %: Nd 11.50. $\text{Nd}(\text{NO}_3)_3 \cdot 2[(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\text{CH}_2)\text{As}]\text{NO}_3$. Calculated %: Nd 11.56.

The neodymium and triphenylbenzylarsonium double nitrate was more difficultly soluble in ethanol than were the other double salts described above. It crystallized from ethanol as coarse crystals with a lilac color. It was readily soluble in cold acetone, methyl alcohol, and a mixture of ethanol and chloroform; it was also soluble in hot 96% alcohol. It was practically insoluble in ethyl ether, chloroform, benzene, toluene, and other hydrocarbons.

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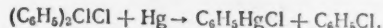
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PHENYLATION REACTIONS BY MEANS OF DIPHENYLBROMONIUM AND DIPHENYLCHLORONIUM SALTS

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and L. S. Isaeva

During heterolytic arylation of bromobenzene and chlorobenzene with aryldiazonium fluoborates, we obtained a number of diarylhalonium salts, among them diphenylbromonium and diphenylchloronium salts [1]. In the present work, we describe a procedure which increases the yield of these salts by a factor of 10 — from 0.6 to 6% of theoretical (calculated on the benzenediazonium fluoborate). An investigation of the chemical properties of the diphenylbromonium and diphenylchloronium salts showed that they are completely analogous to diphenyliodonium salts in their behavior. They are all superior phenylating reagents, capable of phenylating both homolytically (halide salts) and heterolytically. Homolytic phenylation occurs, for example, during the action of all three halonium halides, iodides, chlorides, and bromides, on metallic mercury, best of all in isopropyl alcohol medium, according to:



A remarkable preliminary conclusion to be drawn from the fact of the occurrence of this reaction is that of the existence of a covalent form of diphenylbromonium and diphenylchloronium halides, $(\text{C}_6\text{H}_5)_2\text{Hal} - \text{Hal}$, in which the central halogen atom must expand its octet to ten electrons. This problem will be investigated in the future. As examples of heterolytic phenylation may be cited phenylation of sodium nitrite in aqueous solution by diphenylbromonium and diphenylchloronium halides which forms nitrobenzene, phenylation of potassium cyanide (benzonitrile), of sodium azide (phenyl azide), and of diethylamine (diethylaniline), all of which are described in the present paper. Phenylation by means of diphenylbromonium and diphenylchloronium fluoborates also proceeds heterolytically. These compounds do not require the use of water as the reaction medium. For example, pyridine reacts with diphenylbromonium or -chloronium fluoborate to give N-phenylpyridine fluoborate in 85% yield. Diethylamine is similarly phenylated. In all cases investigated, all three diphenylhalonium compounds behaved identically.

As regards the interaction of diphenylhalonium salts with metals, an interesting peculiarity should be mentioned. Only diphenylhalonium halides react with metallic mercury, forming phenylmercury halides, while the fluoborates do not react, a fact which evidently can be explained by the heterolytic nature of the decomposition of the latter. However, the situation is just the opposite with metallic thallium; a diphenylthallium salt is formed only with halonium fluoborates. The relationship here is completely identical with the results of reactions of diazonium salts with these two metals. It is obvious that the explanations must be the same. A diazonium fluoborate also forms organometallic compounds with lead [2]. In order to explain this result with diazonium salts, we, together with L. G. Makarova [3], proposed that metals, being nucleophilic reagents, can, similarly to the ions OH^- , CN^- , etc., convert the diazonium cation into the diazo form which decomposes homolytically:

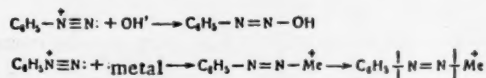


TABLE 1

Reactions of Diphenylbromonium and Diphenylchloronium Salts *

Starting salt g	Reagent, ml or g	Solvent, ml	Reaction conditions	Reaction product		
				Formula	M.p., °C	Yield, %
$[(C_6H_5)_2Br]I^+$ 0.4	Metallic mercury 1.0 ml	$-C_6H_5-OH$ 2.5	Reflux 5-7 min.	$C_6H_5HgI^+$	270.5	29
0.16	1.5 .	1.5	Agitation at room temp. 30 min.	The same	270 (*)	45
3.3	2.0 .	Water 15	Reflux 2 hrs.	. .	270.5	2.4
$[(C_6H_5)_2Br]Br$ 0.3	1.5 .	$-C_6H_5OH$ 3	Agitation at room temp. 30 min.	$C_6H_5HgBr^+$	280 (*)	41
$[(C_6H_5)_2Cl]I^+$	1.5 .	3	Same for 15 min.	$C_6H_5HgI^+$	270	26*
$[(C_6H_5)_2Cl]Br^+$	1.5 .	Aqueous $1-C_6H_5OH$ 3	. . 30 .	$C_6H_5HgBr^+$	280	66*
$[(C_6H_5)_2Cl]Cl^+$	1.5 .	3	. . 30 .	$C_6H_5HgCl^+$	260 (*)	15*
$[(C_6H_5)_2Cl]BF_4$	Metallic thallium 2.4 g	Acetone 15	. . 38 hrs.	$(C_6H_5)_3TlBF_4^+$	—	9.5
$[(C_6H_5)_2Br]BF_4$. . 36 .	The same	—	11.4
$[(C_6H_5)_2I]BF_4$. . 42 .	The same	—	6
$[(C_6H_5)_2Br]BF_4$	4.0 .	25	. . 42 .	The same	—	6
2	Metallic copper 2.0 g	10	. . 3 .	$\{ C_6H_5OH^+ \}$ $C_6H_5-C_6H_5$	69-70	17.5 52
0.91		Water 20	. . 3 .	$\{ C_6H_5OH^+ \}$ $C_6H_5-C_6H_5$	69-70	77 Trace
2		Dry cyclo- hexanone 15	. . 3 .	$\{ C_6H_5OH^+ \}$ $C_6H_5-C_6H_5$	69-70	4 62
$[(C_6H_5)_2Br]I$ 0.8	$NaNO_2$ 2.5	Water 30	Reflux, 3 hrs.	$C_6H_5NO_2^+$		54 ¹¹
$[(C_6H_5)_2Cl]I^+$	1.3 .	15	Same, 1 hr.	The same		31 ¹¹
$[(C_6H_5)_2Br]I$ 1.0	NaN_3 2.5 g	30	. . 3 .	$C_6H_5N_3^+$		55 ¹¹
$[(C_6H_5)_2Cl]I^+$	1.3 .	15	. . 1.5 .	The same		40 ¹¹
$[(C_6H_5)_2Br]I$ 1.6	KCN 3.3 g	120	. . 2 .	$C_6H_5CN^+$		21
3.0	$(C_6H_5)_3NH$ 16 ml	—	. . 5 .	$C_6H_5N(C_6H_5)_2^+$		14.5
3.0	9.0 .	Water 10	. . 5 .	The same		20
$[(C_6H_5)_2Cl]I^+$	7.0 .	8	. . 1.5 .	. .		70.5
$[(C_6H_5)_2Br]BF_4$ 1.5	9.0 .	—	. . 3 .	. .		70
$[(C_6H_5)_2Cl]BF_4$ 0.75	4.5 .	—	. . 3 .	. .		83
0.4	C_6H_5N 1.5 ml	—	Sealed tube 206*	$[C_6H_5NC_6H_5]BF_4^+$	176-177 (11)	85
$[(C_6H_5)_2Br]BF_4$ 0.5	1.5 .	—	The same 213	The same	176.5-177.5	84.5

* This series of experiments was carried out with the assistance of L. V. Lisitskaya.

Notes.

1. Diphenylmercury was obtained by symmetrization with sodium stannite; m. p. 125-125°.

2. Diphenylbromonium and -chloronium fluoborates do not react with metallic mercury.
3. Identified as diphenylmercury with a m. p. of 124-125°.
4. Obtained under the above-described conditions from 0.5 g of diphenylchloronium fluoborate, and in view of its extreme instability, it was introduced into the reaction without preliminary purification.
5. Calculated on diphenylchloronium fluoborate.
6. A solution of 0.2 g of diphenylchloronium fluoborate in the minimum amount of water and saturated with sodium bromide or lithium chloride was introduced into the reaction.
7. Identified as $(C_6H_5)_2TiCl$. (Found %: C 37.00; 36.93; H 2.62, 2.72. $C_{12}H_{10}TiCl$. Calculated %: C 36.58; H 2.56).
8. Identified as $(C_6H_5)_2TiCl$. (Found %: C 36.50, 36.52; H 2.87, 2.95).
9. Identified as tribromophenol, m. p. 92°. A mixture with a known sample showed no m. p. depression.
10. After reduction and diazotization, identified as benzeneazo- β -naphthol, m. p. 128.5-129.5° (128.5-129.5° [10]).
11. Yield given for benzeneazo- β -naphthol calculated on the original salt.
12. Identified as benzoic acid, for which the yield, calculated on diphenylbromonium iodide, is given.
13. Identified as 4'-nitro-4-diethylaminoazobenzene with a m. p. of 150-151.5° (151° [11]), for which the yield, calculated on the original salt, is given.

An analogous explanation for halonium salts would require the formation of a transition complex with metallic mercury in which the diphenylhalonium cation is in a covalent form (with a ten-electron shell):



Mercury, which is sufficiently nucleophilic to bring about the transformation of the diazonium ion into the diazo form, cannot accomplish this transformation with diphenylhalonium ions, while the less noble elements bring about both conversions. That copper, for example causes homolytic decomposition both of diazonium salts (the Gattermann reaction and a number of our works on the synthesis of organometallic compounds by the diazo method [4]) and of halonium salts, as follows from the present work, is confirmation of this point of view. Thus, diphenylbromonium fluoborate forms diphenyl in the presence of copper at room temperature.

All of the enumerated facts can also be explained by heterolytic decomposition of the "onium" compounds with subsequent reduction of the phenyl carbonium ion by the metal to a phenyl radical.

However, the inertness of the triphenyloxonium cation toward metals (as a consequence of the apparent inability of the oxygen to expand its octet to a ten-electron shell), as described in our previous article [5], would appear to confirm the hypothesis presented above.

Data from a crystallographic study and an x-ray analysis of halonium salts will be published by T. L. Khotsyanova. However, it is interesting to note here that diphenylbromonium iodide is isomorphous with diphenyliodonium bromide.

EXPERIMENTAL METHODS

Preparation of diphenylbromonium salts. To 100 ml of bromobenzene at 80-90° (bath temperature) was added, with stirring and over a period of an hour, a solution of 10.8 g of benzenediazonium fluoborate in 300 ml of acetone (the latter distilled during the reaction). The reaction was complete 30 minutes after the addition

of the diazonium solution. After cooling, the combined reaction mixtures from 9 experiments were extracted 4 times with water, and the aqueous extracts were extracted several times with ether. 1.7 g of diphenylbromonium fluoborate was isolated from the first aqueous extract by freezing. 10.2 g of diphenylbromonium iodide (m. p. 81-82° after reprecipitation from CH_3OH with ether) was obtained by the addition of NaI from the 2nd, 3rd, and 4th aqueous extracts (of 100 ml each) and from the residue from the first extract after separation of the $[(\text{C}_6\text{H}_5)_2\text{Br}]\text{BF}_4$.

The diphenylbromonium fluoborate was reprecipitated twice from CH_3OH with ether, and recrystallized from absolute ethanol. This material was in the form of colorless crystals with a decomposition temperature of 120-121°; it was stable at room temperature.

Found %: C 44.97, 44.93; H 3.12, 2.95. $\text{C}_{12}\text{H}_{10}\text{BrBF}_4$. Calculated %: C 44.92; H 3.15.

The total yield of both diphenylbromonium salts was 6.6% of theoretical.

Preparation of diphenylchloronium salts. 0.14 g (1% of theoretical) of diphenylchloronium fluoborate was obtained, under the above-described conditions, from 10.8 g of benzenediazonium fluoborate (in 300 ml of acetone) and 100 ml of chlorobenzene. After reprecipitation from CH_3OH with ether, it decomposed at 109.5-110°, and was in the form of colorless crystals, readily soluble in water, alcohol, and acetone and insoluble in ether.

Found %: C 52.13, 52.09; H 3.76, 3.71. $\text{C}_{12}\text{H}_{10}\text{ClBF}_4$. Calculated %: C 52.12; H 3.65.

On the addition of NaHgI_3 to the residue from the first aqueous extract and to the 2nd, 3rd, and 4th aqueous extracts, 1.05 g of difficultly water-soluble $[(\text{C}_6\text{H}_5)_2\text{Cl}]\text{HgI}_3$ was precipitated; thus the total yield of diphenylchloronium fluoborate was 3.3% of theoretical.

Diphenylchloronium iodide was precipitated by the addition of NaI to a concentrated aqueous solution of diphenylchloronium fluoborate cooled to 0°. After recrystallization from CH_3OH at temperatures in the range of +20 to -70°, the salt was in the form of very unstable colorless crystals with a decomposition temperature of 56-57.5°, readily soluble in water, lower alcohols, and acetone and insoluble in ether.

Found %: C 44.96, 45.11; H 3.27, 3.34. $\text{C}_{12}\text{H}_{10}\text{ClI}$. Calculated %: C 45.52; H 3.16.

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THE EFFECT OF THE COMPOSITION OF THE GAS MIXTURE ON THE YIELD OF CARBONYL COMPOUNDS DURING THE OXIDATION OF PROPYLENE OVER COPPER CATALYST

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(Presented by Academician B. A. Kazansky, August 10, 1957)

The value of acrolein as a raw material for the synthesis of various valuable products has increased in recent years [1]. This increase was connected with the discovery of a new method for the production of acrolein by the direct oxidation of propylene over copper catalysts. However, notwithstanding the considerable number of patents, the publications in the scientific literature devoted to this reaction are very few.

S. Z. Roginsky and co-workers [2] established the highly selective effect of cuprous oxide on the propylene oxidation process. We previously studied the significance of the nature of the catalyst base on this reaction. In the present work, with the aim of determining the optimum conditions for the production of acrolein, we investigated the effect of oxygen concentration in the feed gas on the oxidation of propylene in the presence of copper catalysts.

The reactor in which the oxidation experiments were carried out was a U-shaped glass tube, which was heated to 350° by a molten nitrate mixture. The gas mixture was fed to the catalyst at a space rate of 2000. The carbonyl compounds formed during the reaction were determined as the 2,4-dinitrophenylhydrazones and by titration with hydroxylamine. The acrolein was determined by a spectrophotometric method, developed by us, and involving the use of ultraviolet absorption spectra of aqueous solutions of the carbonyl compounds. The gases formed during the reaction were analyzed in a VTI apparatus. Carbon dioxide was determined in a separate sample by the barium oxide method. The catalyst composition was 1.5% CuO on silicon carbide, and the catalyst was prepared by a method described previously [2].

It is well known [4] that in the study of oxidation reactions, it is frequently difficult to obtain reproducible results owing to instability of the catalyst. In the case of the oxidation of propylene to acrolein this is an especially important consideration, since the selective course of the reaction depends on cuprous oxide which is metastable at 350°. Therefore, in order to obtain reproducible results, prior to the collection of a sample for analysis, a gas mixture of a specified composition was passed for an hour through the catalyst, after which the temperature in the catalyst zone usually became constant. We have provisionally called this operation "conditioning" the catalyst.

In some cases, a gas mixture having a composition different from that used in the experiment was used for the catalyst "conditioning."

The experimental results, which are presented in Table 1, show that an increase in the concentration of oxygen in the oxidizable gas mixture promotes an increase in the yield of carbonyl compounds (calculated on the oxygen), but catalyst stability is decreased at the same time. Thus, for example, at a propylene-to-oxygen ratio of 13:1 (by volume), after passing the gases over the catalyst for three hours, the yield decreased by a factor of 2.5. It was noted that a change in the gas ratio toward an increased concentration of oxygen (for example, during "conditioning" of the catalyst with a 6:1 propylene-oxygen mixture) reduced catalyst activity.

The yield of carbonyl compounds was more stable when the oxidation of the gas mixture was carried out at propylene-to-oxygen ratios of 10:1 and lower. At these ratios, the yield of carbonyl compounds varied from 25.5 to 32.4%, and the volume of carbonyl compounds varied from 104 to 252 g per liter of catalyst per hour. The catalyst operated for 78 hours without regeneration under these conditions.

TABLE 1

Results Obtained During the Oxidation of Propylene Over a Catalyst Consisting of 1.5% CuO on Silicon Carbide with Various Concentrations of Propylene and Oxygen in the Feed Gas

C ₃ H ₆ :O ₂ ratio (by volume)	Yield of carbonyl compounds, %		Volume of carbonyl compounds, g/liter/hr	Tail gas composition, %			
	on oxygen fed	on propylene fed		CO ₂	O ₂	C ₂ H ₄	CO
4:1	23.5	6.2	252.0	—	9.35	—	0.0
4.75:1	23.4	4.8	197.0	3.4	8.0	88.6	0.0
6:1	25.5	4.3	173.0	2.6	2.3	95.1	0.0
7.5:1	28.1	3.8	151.0	2.3	3.1	94.6	0.0
10:1	32.4	3.3	132.0	2.2	3.3	94.5	0.0
13:1	33.7	2.6	104.0	1.4	2.2	96.4	0.0
13:1 (Catalyst "conditioning" with a 6:1 mixture)							
30:1	40.6	3.1	126.0	2.0	1.9	96.1	0.0
(Catalyst "conditioning" with 6:1 mix. 30:1)							
30:1	48.8	1.6	65.8	0.8	0.0	99.2	0.0
(After 2 hrs. operation)							
30:1	38.9	1.3	51.3	0.6	0.0	99.4	0.0
(After 3 hrs. operation)							
30:1	30.6	1.0	39.8	0.6	0.0	99.4	0.0
(After 5 hrs. operation)	18.7	0.6	25.0	0.6	0.5	98.9	0.0

Analysis by the spectrophotometric method showed that 60-70% of the carbonyl compounds was acrolein. For a more detailed investigation, the liquid reaction products were condensed, and, after distillation of the propylene, were given a rough distillation from a Favorsky flask. Fractions having the following boiling ranges at 720 mm Hg were collected:

	Yield, weight, %
Fraction I, 33-49°	8.0
Fraction II, 49-50°	70.0
Fraction III, 50-68.5°	4.2
Residue above 68.5°	15.8
Loss	2.0

During the spectrophotometric investigation, it was established that Fraction I consisted mainly of acrolein (80%), water, and traces of acetone and formaldehyde. As seen from Fig. 1, Fraction II was acrolein. Fraction III contained acrolein and other high-boiling carbonyl compounds. Owing to the small amount of this fraction, it could not be investigated in detail. However, by recrystallization of the 2,4-dinitrophenylhydrazones obtained from Fraction III it was possible to isolate a small amount of osazones (qualitative reaction with alcoholic alkali), which indicated the presence of methylglyoxal. The residue was apparently polymers of acrolein and glyoxal.

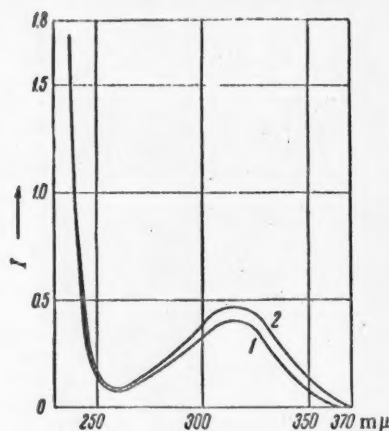


Fig. 1. Absorption curves in the ultraviolet region.
1) Absorption curve of the substance formed during the oxidation of propylene (Fraction II); 2) absorption curve of pure acrolein.

The investigations of the fractions confirmed the data of S. Z. Roginsky [2] relative to the highly selective action of copper catalyst during the oxidation of propylene. An interesting fact is the presence of methylglyoxal in the products of the oxidation of propylene. It should be noted that when acrolein was passed over this catalyst at 350°, no dioxo compounds were formed (negative test for osazones). This indicates that methylglyoxal is not a product of the direct oxidation of acrolein, but is formed during the propylene oxidation process. The formation of pyruvic aldehyde and glyceraldehyde during the cold-flame oxidation of propylene was established by M. B. Neiman and F. A. Lukovnikov [5]. The formation of one of these products during the catalytic oxidation of propylene indicates that this process can be used not only for the synthesis of acrolein, but also for the production of other products.

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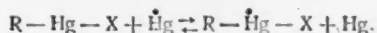
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ISOTOPE EXCHANGE BETWEEN SOME ORGANOMERCURY SALTS AND METALLIC MERCURY TAGGED WITH Hg^{203}

O. A. Reutov and U Yan-tsei

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In the course of a study of the reactivity of various types of metallo-organic compounds in isotope exchange reactions [1, 2], we found that α -mercurized oxo compounds react under mild conditions with metallic mercury tagged with the radioactive isotope Hg^{203} .



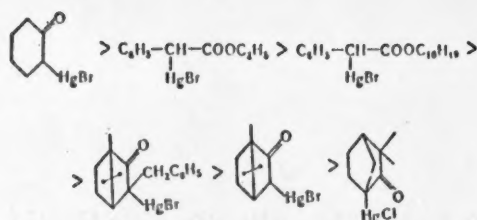
We studied the reaction of metallic mercury with α -bromomercurycyclohexanone, the ethyl ester of α -bromomercuriphenylacetic acid, the L-menthyl ester of α -bromomercuriphenylacetic acid, 3-bromomercuri-3-benzylcamphor, 3-bromomercuricamphor, 1-chloromercuricamphenllone, and also 2-bromomercuricamphane and n-butylmercury bromide.

The reactions of the organomercury salts with metallic mercury were all carried out under the same conditions. All reactions were carried out in the same flask, which was fitted with a reflux condenser, a pipet for sample collection, and a Witt stirrer which rotated at 2500 ± 200 rpm. In all cases, the concentration of organomercury compound was 0.015 mole/liter; the mercury was used in considerable gram-equivalent excess (66-fold or 132-fold). The reactions were carried out in a thermostatted system. Absolute benzene was used as the solvent. However, it was necessary to use dioxane as the solvent for 3-bromomercuricamphor, since this substance is practically insoluble in benzene.

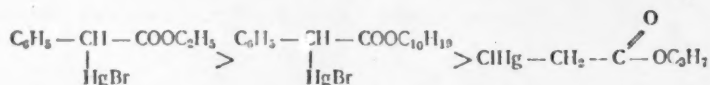
Samples for the determination of the radioactivity of the organomercury compounds were taken from the reaction mixture at specific times. Along with the sample some colloidal metallic mercury was always obtained, from which the sample was freed by passage through a chromatographic column containing aluminum oxide. The solution of organomercury compound was then evaporated to dryness under a stream of dry air, and the substance was recrystallized from an appropriate solvent until constant radioactivity and the literature melting point were attained. Measurements of the radioactivity of the organomercury compounds were carried out in a B-2 apparatus with the aid of MST-17 end window counters and MS-4 γ counters by the method previously described [2].

Special experiments showed that reproducibility of results was completely satisfactory in spite of the heterogeneous nature of the reaction. Divergence of the results of identical experiments carried out at different times did not exceed 10%.

In Table 1 are presented the results of our experiments on isotope exchange between various organomercury compounds and metallic mercury tagged with Hg^{203} . From the table it is seen that the reactivity of α -mercurized oxo compounds toward metallic mercury decreases in the series:



Reserving the right to return to a detailed analysis of these results, we note that the reactivity of these organomercury salts toward metallic mercury is determined not only by the electronic character of the radicals at the carbon atom bound to the mercury, but also, unconditionally, in a number of cases, by steric factors. That is precisely why, probably, the L-menthyl ester of α -bromomercuriphenylacetic acid reacts more slowly than the corresponding ethyl ester. On the other hand, from a comparison of the reactivities of esters of α -bromomercuriphenylacetic acid and of the n-propyl ester of α -chloromercuriacetic acid (does not react with Hg^{203} at 23°)



It is apparent that the activating effect of the phenyl radical predominates over the steric hindrance it creates.

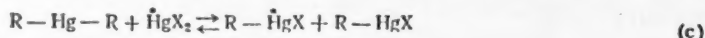
1-Chloromercuricamphenilone, like 2-bromomercuricamphane and n-butylmercury bromide which are not α -mercury derivatives of oxo compounds, does not react with metallic mercury, even on heating at 100° for 40 hours. The high degree of inertness of the mercury atom in 1-chloromercuricamphenilone, observable in many other substitution reactions, has still not been satisfactorily explained. Apparently, our isotope exchange reaction is homolytic.

Since during a study of certain symmetrization reactions of organomercury salts [3, 4] it was established that the symmetrizing agent (NH_3 , KI) does not attack the $\text{R}-\text{HgX}$ molecule but bonds with the HgX_2 molecule formed as the result of the reaction



It is natural to inquire whether such an equilibrium does not play the determining role in our case.


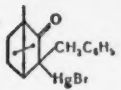



Indeed, it is possible to present the following mechanism for the isotope exchange reaction under consideration:



However, such a scheme is contrary to two experimental facts. The first of these is that some organomercury salts react with metallic mercury under milder conditions than they do with a mercury halide. Thus, for example, the ethyl ester of α -bromomercuriphenylacetic acid readily reacts with Hg in benzene in the cold, but it does not react with $\dot{\text{HgBr}}_2$ under these conditions.

TABLE 1

Results of Isotope Exchange Between Organomercury Salts and Metallic Mercury

Formula of the organo- mercury compound	Expt. No.	Percent exchange at various times											
		0.5 hr.	1.0 hr.	2.0 hrs.	3.0 hrs.	4.0 hrs.	5.0 hrs.	6.0 hrs.	6.5 hrs.	10.0 hrs.	15.0 hrs.	20.0 hrs.	40.0 hrs.
	1	—	81	98	99	—	—	—	—	—	—	—	—
$\text{C}_6\text{H}_5\text{—CH—COOC}_2\text{H}_5$ HgBr	2	16	51	83	91	98	100	—	—	—	—	—	—
$\text{C}_6\text{H}_5\text{—CH—COOC}_{10}\text{H}_{19}$ HgBr	3	2	8	45	60	76	—	—	84	93	—	—	—
	4	—	—	—	—	—	—	—	—	—	39	—	—
	5	—	—	—	—	—	—	—	—	—	—	17	—
	6	—	—	—	—	—	—	—	—	—	—	0	0
	7	—	—	—	—	—	—	—	—	—	—	0	0
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—HgBr}$	8	—	—	—	—	—	—	—	—	—	—	—	0

Notes. 1. The concentration of organomercury compound was 0.015 mole/liter in all experiments. In Experiments Nos. 1-3, the mercury was in 66-fold excess; in Experiments 4-8 it was in 132-fold excess. Dioxane was used as the solvent in Experiment No. 5, while in all remaining experiments the solvent was benzene. Experiments Nos. 1-6 were carried out at 23°, Experiments Nos. 7 and 8 at 80°.

2. All values in the table are percent of equilibrium.

The second fact is that the formation of even traces of mercurous halides was not observed in any of the cases studied by us. And, furthermore, if the reaction did proceed through Equilibrium (a), a certain amount of mercurous halide (together with the symmetrical organomercury compound) would inevitably have to be formed owing to the reaction:



Thus, this isotope exchange reaction does not proceed through Equilibrium (a); rather, the metallic mercury reacts directly with the organomercury salt R—HgX .

Although the reaction is probably homolytic, it hardly proceeds through a stage in which free radicals arise. Isotope exchange proceeds in the cold under conditions of such mildness as have never been associated with the free radical decomposition of organomercury compounds.

That the isotope exchange proceeds with retention of the stereochemical configuration at the carbon atom connected to the mercury atom also indicates that free radicals are not formed. This fact was established by us for the diastereoisomeric L-menthyl esters of α -bromomercuriphenylacetic acid and also for cis- and trans- 2-methoxycyclohexylmercury chlorides.

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PRODUCTION OF XYLENES BY DEALKYLATION AND CONJUGATE
ALKYLATION OF AROMATIC HYDROCARBONS
IN THE PRESENCE OF SYNTHETIC ALUMINOSILICATES

Academician A. V. Topchiev and G. M. Mamedaliev

In a preceding paper [1], we reported the results of our experimental investigations of the synthesis of xylenes by dealkylation of polymethylbenzenes and alkylation of toluene over aluminosilicates. Coke-oven solvent is distinguished by a high content of polyalkylaromatic compounds, and the development of a rational method for the conversion of these compounds into valuable, low-molecular-weight aromatic hydrocarbons is of practical interest.

Composition by fractions, %

Initial b. p. 149°	
149-160°	2.84
160-165°	20.15
165-175°	52.51
175-185°	9.25
185-195°	5.75
Residue	7.20
Loss	2.8

Basic data on a process for the catalytic treatment of a mixture of solvent and toluene over synthetic aluminosilicates are presented in the present communication. The solvent, which was mainly a mixture of polyalkylbenzenes, also contained a certain amount of xylenes and some toluene. A fraction boiling above 150° was separated from it, and this fraction was then used in the experimental work. This polyalkylaromatic fraction of solvent boiled in the range 149-195°. Characteristics of the solvent follow: d_4^{20} 0.8818; n_D^{20} 1.5009; iodine number 20.3; mol. wt. 123; 100% sulfonatable.

The major part (about 73%) of the 149-195° fraction of the solvent was a 160-175° fraction, which consisted mainly of a mixture of pseudocumene and mesitylene. The increased iodine number was due to the presence in the product of a small amount of styrene and indene derivatives. As the second component was used standard toluene with a boiling range of 109-111°, d_4^{20} 0.8675, n_D^{20} 1.4966, 100% sulfonatable, bromine number 0.2. The major part of the experiments was carried out under pressure in a laboratory flow-type apparatus. A schematic diagram and description of this apparatus was published earlier [1].

Separate experiments were carried out at atmospheric pressure in a Pyrex glass reactor with a fluidized layer of microspheroidal and powdered aluminosilicate catalyst. This system was very convenient for conducting the experimental work, and permitted direct observation of the course of the process in glass and the accurate measurement of the parameters of the process. The reactor was heated electrically by means of nichrome wire coiled around it. Yield for a given temperature regime was attained in 10-15 minutes. Constant temperature, varying not more than $\pm 1.0^\circ$, was established at all heights of the fluidized layer in the reactor. This system, which is recommended as a laboratory reactor (Fig. 1), is distinguished by great convenience, and can be used for investigations over wide temperature intervals.

The experiments were carried out with a mixture of solvent and toluene in a weight ratio of 1:2. The effects of pressure, rate, temperature, and length of reaction cycle were studied, and optimum process conditions were determined for xylene production. Only a small amount of xylenes was formed at temperatures below 350°. Toluene did not appreciably participate in the reaction, and only a small decrease in its amount occurred during the process.

TABLE 1
Characteristics of the Products from the Catalytic Treatment of a Mixture of Coke-Oven Solvent and Toluene.

Product characteristics	Feed (wt. ratio of solvent to toluene 1:2)		Catalyzate			
			Press. 1 atm. temp. 480°, space rate 0.5:1 (Expt. 74)		Press. 15 atm. temp. 480°, space rate 0.5:1 (Expt. 63)	
	yield of fractions, wt. %	n_D^{20}	yield of fractions, wt. %	n_D^{20}	yield of fractions, wt. %	n_D^{20}
init. b.p., °C	104.0		66.0		45.0	
<50	—	—	—	—	—	—
50-76	—	—	0.20	1.4509	0.85	1.4868
76-78	—	—	0.10	—	0.37	1.4840
78-83	—	—	1.50	1.4957	6.94	1.4982
83-88	—	—	0.28	1.4901	0.23	1.4981
88-103	—	—	0.71	1.4963	0.80	1.4946
103-108	0.45	1.4962	0.35	1.4969	0.47	1.4961
108-113	64.88	1.4970	63.08	1.4972	48.74	1.4934
113-118	0.13	1.4928	0.22	1.4947	0.27	1.4945
118-125	0.20	1.4912	0.22	1.4918	0.40	1.4944
125-136	0.23	1.4898	0.72	1.4956	1.10	1.4958
136-144	0.22	1.4882	9.37	1.4965	26.92	1.4981
144-149	0.20	1.4868	0.56	1.4971	0.64	1.5011
149-160	1.59	1.4873	1.10	1.4921	1.35	1.4969
160-165	5.03	1.4921	1.99	1.4919	3.35	1.4959
165-175	20.29	1.4688	12.49	1.4979	4.65	1.4992
175-185	2.32	1.5008	1.49	1.4959	0.80	1.4988
185-200	1.99	1.4970	—	—	0.37	1.5010
end point, °C	194.5		185.0		190.0	
Over-all yield, wt. %	97.53		94.38		97.83	
Residue, wt. %	1.90		4.20		2.01	
Loss, wt. %	0.57		1.42		0.16	
d_4^{20}	0.8689		0.8670		0.8675	
n_D^{20}	1.4981		1.4988		1.4991	
Iodine No.	7.7		3.6		2.5	
% Sulfonatable	100		100		100	
Group chem. compn. wt. %						
Unsaturation	3.8		1.8		1.5	
Aromatics	96.2		98.2		98.5	
Naphthenes + Paraffins	—		—		—	
Material balance, wt. %						
Catalyzate	—		94.5		87.8	
Coke	—		1.8		4.8	
Gas	—		1.2		4.2	
Loss	—		2.5		3.2	

TABLE 2
Characteristics of the Major Aromatic Fractions

Product characteristics	Feed mixture	Catalyzate, Expt. 74	Catalyzate, Expt. 63	Product characteristics	Feed mixture	Catalyzate, Expt. 74	Catalyzate, Expt. 63
78-83° Fraction				n_D^{20}	1.4970	1.4972	1.4964
Yield, wt. %	—	1.50	6.94	% Sulfonatable	100	100	100
d_4^{20}	—	0.8736	0.8739	Bromine No.	0.08	0.08	0.08
n_D^{20}	—	1.4957	1.4982	136-144° Fraction			
% Sulfonatable	—	—	100	Yield wt. %	0.22	9.37	26.92
Bromine No.	—	—	0.32	d_4^{20}	—	0.8664	0.8653
136-144° Fraction				n_D^{20}	1.4882	1.4975	1.4981
Yield wt. %	64.88	63.08	48.74	% Sulfonatable	—	100	100
d_4^{20}	0.8653	0.8666	0.8668	Bromine No.	—	0.16	0.08

A more marked dealkylation of the original polyalkylbenzenes was observed at temperatures of 450-480°. In Tables 1 and 2 are presented analytical data for two characteristic catalyzates and their

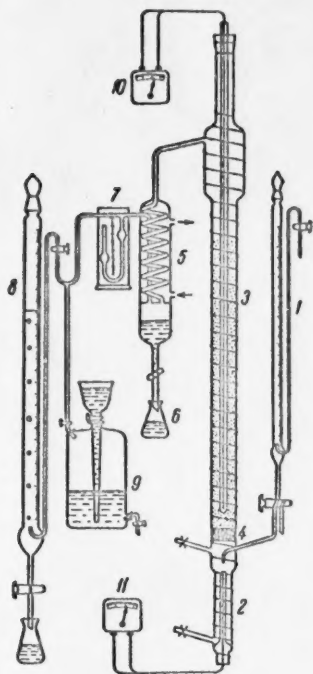


Fig. 1. Laboratory flow-type apparatus using a fluidized layer of microspheroidal and powdered catalyst. 1) Feed buret; 2) vaporizer; 3) reactor; 4) glass filter; 5) cooler-condenser; 6) receiver; 7) flow meter; 8) buret for gas collection; 9) gasometer; 10, 11) galvanometers.

formation of xylenes. A part of the polyalkylbenzenes are dealkylated over aluminosilicate with the formation of low-molecular-weight aromatic hydrocarbons and gas.

The synthesis of xylenes by the dealkylation of polyalkylaromatic hydrocarbons and conjugate alkylation of toluene in the presence of synthetic aluminosilicates is a promising process, and its practical application would permit a considerable increase in para-xylene resources and the resources of other valuable low-molecular weight aromatic hydrocarbons.

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major aromatic fractions. The use of pressure had a decisive effect. Thus, at atmospheric pressure and a temperature of 480°, 1.5% benzene and 9.3% xylenes were obtained from the dealkylation of solvent hydrocarbons; an increase in pressure directed the course of the reaction toward maximum formation of xylenes. The catalyzate obtained at 15 atm, and 480° was characterized by a content of 28% xylenes and about 7% benzene. The yields, based on the feed, of catalyzate, gas and coke were, respectively, 88, 4.8, and 4.2 wt. %. The gaseous reaction products consisted of a mixture of methane and its homologs and hydrogen. Deep conversion of the solvent hydrocarbons was observed. Part of the toluene was alkylated with the formation of xylenes, which resulted in a decrease in the amount of it from 64% in the feed to 48% in the catalyzate. As seen from Table 2, the aromatic fractions obtained under optimum conditions contained practically no unsaturated, paraffinic, or naphthenic hydrocarbons; their bromine number varied in the range 0.08-0.3, and they were 100% sulfonatable. Spectral analysis of the xylene fraction of the catalyzate showed for it a content of about 25% p-xylene, 45-50% m-xylene, about 20-25% o-xylene, and an insignificant amount of ethylbenzene (not more than 2-3%).

The process of catalytic treatment of a mixture of solvent and toluene is characterized by the simultaneous occurrence of the reactions of dealkylation and conjugate alkylation of the original aromatic hydrocarbons. In addition to these reactions, evidently a certain amount of toluene disproportionation also participates in the

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CONTINUOUS HYDROCHLORINATION OF ACETYLENE OVER ALUMINUM OXIDE

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(Presented by Academician S. I. Volfkovich, July 18, 1957)

Acetylene, possessing a very high reactivity, adds hydrogen chloride with the formation of vinyl chloride. As is well known, the latter is readily polymerized and copolymerized to plastic products.

At the present time, the basic raw materials for the industrial production of vinyl chloride are dichloroethane and acetylene. Correspondingly, there are two basic production methods in industry [1-5]. The method in which dichloroethane is dehydrochlorinated by an alcoholic solution of alkali came into technical use, and has attained great significance up to the present; this method is used in the U.S.A.

A second important method for the production of vinyl chloride, which was developed in Germany, is the addition of hydrogen chloride to acetylene. This reaction is carried out either in the gas phase or in a liquid medium. When the reaction is carried out in the gas phase, the catalyst is mercuric chloride on porous carriers. When the reaction is carried out in the liquid phase, cuprous chloride is used.

The most economically advantageous method for the production of vinyl chloride is the first. However, the great drawbacks of operating with mercury catalysts has induced investigators to search for economically feasible catalysts which do not contain mercury.

In the present communication, data from a laboratory investigation of the use of aluminum oxide for the hydrochlorination of acetylene are reported.

Vinyl chloride was obtained by the authors by reacting acetylene and hydrogen chloride over aluminum oxide in a flow system in the temperature range 250-350°. The effect of the following variables on the addition of hydrogen chloride to acetylene was investigated: 1) pre-treatment of the catalyst with hydrogen chloride, 2) concentration of hydrogen chloride in the feed gas, and 3) temperature.

The experiments on the hydrochlorination of acetylene were carried out in the usual flow-type apparatus using commercial aluminum oxide. Acetylene and hydrogen chloride, which had been previously purified and dried, were passed through a mixer into the catalyst tube.

The product gas, comprising vinyl chloride and unreacted acetylene, was collected in a Patrikeev gasometer system with automatic pressure control. A third component — hydrogen chloride — was absorbed in water upstream of the collection system. The content of vinyl chloride in the product gas was determined by molecular weight, and was recalculated into terms of yield based on acetylene.

In addition, simultaneously with the hydrochlorination reaction, partial decomposition of the acetylene to hydrogen and carbon occurred accompanied by carbon deposition on the catalyst; the latter was determined from the CO₂ produced during regeneration of the catalyst. Hydrogen was found in the product gas, but in very small amounts in comparison with that which would be calculated from the carbon deposition. Therefore,

the yield of vinyl chloride was determined, as indicated above, on the basis of the two-component system, acetylene - vinyl chloride.*

TABLE 1

Expt. No.	HCl treatment of Al_2O_3		Mol. wt. of product gases	Yield of vinyl chloride	Carbon deposition
	Duration, hours	Reactor temp. °C		in μ of acetylene	
1	Without pretreatment		41.44	42.3	10.6
3	9	20	43.63	48.3	9.1
5	7	300	40.70	40.3	not det.
19 (repeat)	3	200-300	47.56	59.1	9.1

It was shown experimentally that the yield of vinyl chloride materially depends on pre-treatment of the catalyst with hydrogen chloride and on the conditions under which the pre-treatment is carried out. In Table 1 are presented experiments: a) without pre-treatment of the catalyst with hydrogen chloride (Experiment 1); b) pre-treatment by passing hydrogen chloride through the catalyst at room temperature for 9 hours and subsequently raising the temperature to reaction temperature (Experiment 3); c) the same, but the temperature was simultaneously raised from room temperature to 300° over a period of 3 hours (Experiment 19).

TABLE 2

Expt. No.	Acetylene: hydrogen chloride	HCl in feed gas, %	Mol. wt. of product gas	Yield of vinyl chloride	Carbon deposition	HCl removed from catalyst after the reaction, ml per g catalyst
				in % of acetylene		
8	1:0.60	37.5	39.21	36.2	11.0	4.2
7	1:1	50.0	42.13	44.2	not det.	8.1
19	1:1.25	55.5	47.56	59.1	9.1	12.9
9	1:1.85	65.0	48.29	61.1	not det.	31.6
12	1:2.60	72.0	48.92	62.8	3.7	118.5

The experiments were carried out at 300°; the catalyst charge was 50 ml (bulk density 0.53 g/ml). Acetylene was fed to the reactor at a rate of 2.1 liters/hour; the hydrogen chloride rate was 2.3-2.4 liters/hour.

It is seen from Table 1 that pre-treatment of the catalyst with hydrogen chloride increased the yield of vinyl chloride to 59% for a three-hour pretreatment of the catalyst while simultaneously bringing the reactor up to reaction temperature.

The study of the effect of hydrogen chloride concentration in the feed gas on the formation of vinyl chloride was carried out at ratios of acetylene to hydrogen chloride of 1:0.6 to 1:2.6.

* The formation of up to 0.5 ml of liquid products which condensed in two layers was observed in the majority of experiments. The lower layer corresponded to a 10-15% solution of HCl, while the upper layer was a mixture of chloro derivatives of acetylene. These products were not investigated in detail, and were not taken into consideration due to their insignificant quantity.

The experimental results are presented in Table 2.

It is seen from Table 2 that with the hydrogen chloride present in the gas mixture in very small excess over the stoichiometric ratio (5.5%, Experiment 19), the yield of vinyl chloride was sharply increased (59.1%). With approximately a 4-fold increase in excess HCl (22%, Experiment 12), there was no further significant increase in the yield of vinyl chloride (62.8%).

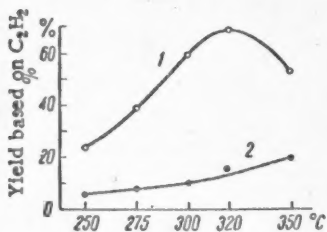


Fig. 1

equilibrium for the hydrochlorination of acetylene at room temperature is completely shifted toward the vinyl chloride side. With an increase in temperature, owing to the exothermic nature of the process, the equilibrium shifts to the left. However, in the temperature interval 250-350°, the equilibrium constant is still sufficiently high, and changes from $3 \cdot 10^4$ to $4.6 \cdot 10^2$. We studied the effect of temperature on the formation of vinyl chloride in this temperature range (see Fig. 1, 1); data were also obtained on the change in carbon deposition in this same temperature interval (Fig. 1).

As seen from Fig. 1, the yield of vinyl chloride increased with temperature, and the maximum yield (approximately 70%) lay in the range of 300-320°. The yield at 350° was lower than at 300°. In these experiments, the acetylene was fed at a rate of 1.9-2.1 and 4.1 liters/hour (at 320°), and the ratio of acetylene to hydrogen chloride was 1:1.25. Under these conditions, the activity of the catalyst did not change over a period of 4 hours, which is sufficient for kinetic investigations of the process; these are being carried out at the present time.

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